

# Does the Oxygen Functionality Really Improve the Thermodynamics of Reversible Hydrogen Storage with Liquid Organic Hydrogen Carriers?

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## Materials

The samples used in this work were of commercial origin (see Table S1).

### Table S1.

Provenance and purity of the materials

Material	CAS	Origin	GC purity (mass fraction) <sup>a</sup>
benzyl-phenyl ether (cr)	946-80-5	Sigma-Aldrich	0.9998
dibenzyl ether (liq)	103-50-4	Sigma-Aldrich	0.9997
2-methoxy-naphthalene (cr)	93-04-9	Acros	0.9987

<sup>a</sup> The final purity after purification, determined by GC.

Samples for combustion calorimetry were purified using fractional sublimation or fractional distillation. The final purities of the samples were determined by GC. The samples were analysed with a Hewlett Packard 5890 II series gas chromatograph equipped with a flame ionisation detector and an HP-5 capillary column (length, inside diameter, and film thickness of 25 m×0.32 mm×0.25 μm). The GC temperature program started at  $T = 323$  K, followed by heating at a rate of  $0.167$  K·s<sup>-1</sup> to  $T = 573$  K. The water contents of samples were determined by Karl Fischer titration using a Metrohm 756/831 KF Coulometer. Results of the KF titrations are given in Table S2. Before starting the vapour pressure measurements, the samples were preconditioned in the transpiration saturator (see below for details).

## Combustion calorimetry: enthalpy of formation determination

The standard molar energy of combustion was measured with a self-made high-precision isoperibolic calorimeter with a static bomb and a stirred water bath. About 0.3-0.5 g of the solid sample was pressed into a pellet, weighed with a microbalance with a

resolution of  $10^{-6}$  g, and burned in oxygen at a pressure of 3.04 MPa. In a preliminary series of combustion experiments, a considerable amount of soot was sometimes observed on the walls of the Pt crucible. To achieve complete combustion, a certain amount of polyethylene cuttings was used as an auxiliary compound. The pellet was placed in the crucible, surrounded with polyethylene cuts and ignited. The clean experiments with and without polyethylene showed results that agreed within the experimental uncertainty. The bomb was not purged with oxygen beforehand. Test experiments with and without purging with  $O_2$  showed results that were also consistent within the experimental uncertainty. The detailed procedure has already been described [1,2].

The liquid sample was transferred (in the glove box) with a syringe into the polyethylene bulb (Fa. NeoLab, Heidelberg, Germany). The neck of the bulb was compressed with special tweezers and sealed by heating the neck near a glowing wire. The bulb with the liquid sample was placed in the crucible and burnt in oxygen at a pressure of 3.04 MPa.

The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but neither was detected. The energy equivalent of the calorimeter  $calor$  was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T.). Correction for nitric acid formation was based on titration with  $0.1 \text{ mol}\cdot\text{dm}^{-3}$  NaOH (aq). Conventional procedures [3] were used for reduction of the data to standard conditions. Auxiliary data required for the reduction are collected in Table S2.

**Table S2**

Auxiliary quantities: formula, density  $\rho$  (293 K), massic heat capacity  $c_p$ (298.15 K), and expansion coefficients  $(\alpha/V/T)_p$  of the materials used in the present study<sup>a</sup>

Compounds	Formula	Water content <sup>b</sup> ppm	(293 K)	$c_p$ (298.15 K)	$(\alpha/V/T)_p$ <sup>c</sup>
			$\text{g}\cdot\text{cm}^{-3}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}$	$10^{-3}\cdot\text{cm}^3\cdot\text{K}^{-1}\cdot\text{g}^{-1}$
benzyl phenyl ether (cr)	$C_{13}H_{12}O$	84.3	1.06 <sup>d</sup>	1.29 <sup>e</sup>	0.1
dibenzyl ether (liq)	$C_{14}H_{14}O$	75.2	1.04 <sup>d</sup>	1.72 <sup>e</sup>	1.0
polyethylene <sup>c</sup>	$CH_{1.93}$		0.92	2.53	0.1
cotton <sup>c</sup>	$CH_{1.774}O_{0.887}$		1.50	1.67	0.1

<sup>a</sup> Data for the densities,  $\rho$  (293 K), and the specific heat capacities,  $c_p$  (298.15 K), of auxiliary materials are from our previous work [4]. The specific energy of combustion  $\Delta_c u^0$  (cotton) =  $-16945.2 \text{ J}\cdot\text{g}^{-1}$ ;  $u(\Delta_c u^0) = 4.2 \text{ J}\cdot\text{g}^{-1}$ . The specific energy of combustion  $\Delta_c u^0$  (polyethylene) =  $-46357.3 \text{ J}\cdot\text{g}^{-1}$ ;  $u(\Delta_c u^0) = 3.5 \text{ J}\cdot\text{g}^{-1}$ . The standard uncertainties are reported for the specific energies of combustion.

<sup>b</sup> The results of combustion experiments were corrected for this residual amount of water.

<sup>c</sup> Estimated.

<sup>d</sup> Calculated at 293 K using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2024 ACD/Labs) with uncertainty  $\pm 0.06 \text{ g}/\text{cm}^3$

<sup>e</sup> Calculated from the molar heat capacity at 298.15 K (see Table S6).

### *Transpiration method: Vapour pressure measurements*

Absolute vapour pressures were measured using the transpiration method [5,6]. The main idea of this method is to saturate the gas stream flowing over the sample and to determine the amount of compound transferred by the gas within a given time. Approximately 0.5 to 0.8 g of the sample is mixed with glass beads (diameter 1 mm) and placed in the thermostatted U-shaped saturator. The glass beads are needed to enlarge the contact area between gas and sample. A stream of nitrogen at a well-defined flow rate was passed through the saturator at constant temperature ( $\pm 0.1$  K) maintained by Julabo FP51-SL refrigerated circulator, and the transported material was collected in a cold trap. The amount of condensed substance was usually determined by GC using a suitable n-alkane as an internal standard. The saturation vapour pressure  $p_i$  at each temperature  $T_i$  was calculated from the amount of condensate collected within a definite period of time:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i ; \quad V = (n_{N_2} + n_i) \cdot R \cdot T_a / P_a \quad (S1)$$

where  $V$  is the volume of the gas phase consisting of the  $n_{N_2}$  moles of the carrier gas and  $n_i$  mole of gaseous compound under study (with the molar mass  $M_i$ ) at the atmospheric pressure  $P_a$  and the ambient temperature  $T_a$ . The volume of the carrier gas  $V_{N_2}$  was determined by the digital flow rate sensor from integration with a microcontroller. We used the Honeywell S&C - HAFBLF0200C2AX5 digital flow rate sensor with uncertainty at the level of 2.5 %. The flow rate of the nitrogen stream was also controlled by using a soap bubble flow meter (HP soap film flowmeter (model 0101-0113)) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The volume of the carrier gas  $V_{N_2}$  was read from the digital flow sensor. The amount of the compound under investigation  $n_i$  in the carrier gas was estimated at each temperature using the ideal gas law.

Before starting the vapour pressure measurements, the sample was first pre-conditioned at 310-320 K (within about one hour) in order to remove possible traces of water. The saturator was then kept at 310-315 K (to remove possible traces of volatile compounds). To ensure that preconditioning was completed at the selected temperature, three samples were taken sequentially during sample rinsing and analyzed by GC. A constant vapour pressure at this temperature indicated that the transpiration experiments could begin. GC analysis of the transported material did not reveal any additional contamination. The absence of impurities and decomposition products was re-checked by GC analysis of the saturator content at the end of the entire series of experiments.

The procedure for calculating the expanded uncertainties (0.95 level of confidence) of the vaporization enthalpies from the transpiration method includes uncertainties from the experimental transpiration conditions, uncertainties in the vapor pressure and uncertainties in the temperature adjustment to  $T = 298.15$  K, as described elsewhere [7,8].

The uncertainties of the  $\Delta_1^{\text{g}}H_m^{\circ}(298.15 \text{ K})$ -values derived from the vapor pressures reported in the literature include uncertainties from the fitting equation and uncertainties from temperature adjustment to the reference temperature. Uncertainties in the temperature adjustment of vaporization enthalpies to  $T = 298.15$  K are estimated to account with 20% to the total adjustment.

## Absolute vapour pressures

The experimental absolute vapour pressures measured in this work are given in Table S3.

**Table S3.** Absolute vapour pressures  $p$ , and standard molar vaporisation enthalpies and entropies determined using the transpiration method

$T/$ K <sup>a</sup>	$m/$ mg <sup>b</sup>	$V(N_2)^c /$ dm <sup>3</sup>	$T_a/$ K <sup>d</sup>	Flow/ dm <sup>3</sup> ·h <sup>-1</sup>	$p/$ Pa <sup>e</sup>	$u(p)/$ Pa <sup>f</sup>	$\Delta_1^g H_m^o/$ kJ·mol <sup>-1</sup>	$\Delta_1^g S_m^o/$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
benzyl phenyl ether (liq) [946-80-5]								
$\Delta_1^g H_m^o(298.15 \text{ K}) = (73.8 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$								
$\Delta_1^g S_m^o(298.15 \text{ K}) = (142.2 \pm 1.1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$								
$\Delta_1^g G_m^o(298.15 \text{ K}) = (31.4 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p/p_{\text{ref}}) = \frac{316.1}{R} - \frac{97119.2}{RT} - \frac{78.2}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$								
318.3	0.83	5.513	295.7	3.85	2.01	0.06	72.2	137.0
323.1	0.72	3.205	295.7	3.85	3.02	0.08	71.9	135.9
328.2	0.99	2.885	295.7	3.85	4.58	0.12	71.5	134.7
333.2	0.89	1.731	295.7	3.85	6.85	0.20	71.1	133.6
338.4	0.87	1.154	295.7	3.85	10.10	0.28	70.7	132.3
343.2	1.11	1.026	295.7	3.85	14.46	0.39	70.3	131.3
348.1	1.22	0.774	295.7	1.26	20.99	0.55	69.9	130.4
353.2	0.71	0.335	295.7	1.26	28.30	0.73	69.5	128.9
358.1	0.92	0.314	295.7	1.26	38.95	1.00	69.1	127.8
363.2	1.28	0.314	295.7	1.26	54.21	1.38	68.7	126.7
dibenzyl ether (liq) [103-50-4]								
$\Delta_1^g H_m^o(298.15 \text{ K}) = (78.6 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$								
$\Delta_1^g S_m^o(298.15 \text{ K}) = (151.8 \pm 1.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$								
$\Delta_1^g G_m^o(298.15 \text{ K}) = (33.3 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p/p_{\text{ref}}) = \frac{334.0}{R} - \frac{104392.3}{RT} - \frac{86.5}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$								
309.4	0.85	22.97	295.0	9.28	0.46	0.02	77.6	148.8
313.2	0.72	13.61	295.0	9.28	0.66	0.02	77.3	147.7
318.3	0.68	8.017	295.0	10.00	1.05	0.03	76.9	146.2
321.2	0.45	4.279	295.0	7.90	1.31	0.04	76.6	145.1
323.2	0.23	1.767	295.0	4.82	1.61	0.05	76.4	144.8
326.2	0.74	4.477	295.0	7.90	2.04	0.06	76.2	143.8
328.2	0.50	2.410	295.0	4.82	2.59	0.07	76.0	143.8
331.1	1.02	4.016	295.0	7.90	3.15	0.08	75.8	142.6
333.1	0.51	1.646	295.0	4.82	3.86	0.10	75.6	142.5
335.1	0.93	2.633	295.0	7.90	4.36	0.11	75.4	141.6
338.3	1.20	2.530	295.0	4.82	5.87	0.17	75.1	141.1
343.1	1.36	2.016	295.0	4.82	8.32	0.23	74.7	139.7
348.2	1.63	1.606	295.0	4.82	12.51	0.34	74.3	138.6

353.1	2.29	1.646	295.0	4.82	17.22	0.46	73.9	137.1
358.1	3.08	1.566	295.0	4.82	24.28	0.63	73.4	135.9

2-methoxy-naphthalene (liq) [93-04-9]

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (69.9 \pm 0.6) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{l}}^{\text{g}}S_{\text{m}}^{\circ}(298.15 \text{ K}) = (137.9 \pm 1.6) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{l}}^{\text{g}}G_{\text{m}}^{\circ}(298.15 \text{ K}) = (28.5 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{291.5}{R} - \frac{86908.3}{RT} - \frac{57.9}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

348.7	0.99	0.282	296.1	1.06	54.51	1.39	66.7	128.9
350.6	1.05	0.264	296.1	1.06	61.53	1.56	66.6	128.5
353.2	0.98	0.211	296.1	1.06	72.07	1.83	66.5	128.0
356.3	1.19	0.211	296.1	1.06	87.76	2.22	66.3	127.5
359.2	1.42	0.211	296.1	1.06	104.65	2.64	66.1	127.0
362.3	1.42	0.176	296.1	1.06	125.55	3.16	65.9	126.5
365.3	1.37	0.141	296.1	1.06	151.47	3.81	65.8	126.1
368.4	1.67	0.141	296.1	1.06	184.00	4.63	65.6	125.7
372.4	1.59	0.106	296.1	1.06	233.16	5.85	65.3	125.1

2-methoxy-naphthalene (cr) [93-04-9]

$$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (90.4 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{cr}}^{\text{g}}S_{\text{m}}^{\circ}(298.15 \text{ K}) = (198.4 \pm 1.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_{\text{cr}}^{\text{g}}G_{\text{m}}^{\circ}(298.15 \text{ K}) = (31.3 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{325.3}{R} - \frac{99738.0}{RT} - \frac{31.2}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

297.5	0.73	37.08	295.8	3.12	0.31	0.01	90.5	198.5
308.2	0.63	8.979	295.8	4.31	1.08	0.03	90.1	197.4
314.2	1.03	7.650	295.8	4.31	2.10	0.06	89.9	196.7
318.2	1.32	6.609	295.8	4.31	3.10	0.08	89.8	196.0
323.2	1.59	4.454	295.8	4.31	5.57	0.16	89.7	196.0
329.3	1.45	2.191	295.8	4.31	10.26	0.28	89.5	195.4
333.4	0.98	1.006	295.8	4.31	15.10	0.40	89.3	194.8
338.4	1.03	0.647	295.8	4.31	24.73	0.64	89.2	194.5
342.4	1.14	0.503	295.8	4.31	35.31	0.91	89.1	194.0

<sup>a</sup> Saturation temperature measured with the standard uncertainty ( $u(T) = 0.1 \text{ K}$ ).

<sup>b</sup> Mass of transferred sample condensed at  $T = 243 \text{ K}$ .

<sup>c</sup> Volume of nitrogen ( $u(V) = 0.005 \text{ dm}^3$ ) used to transfer  $m$  ( $u(m) = 0.0001 \text{ g}$ ) of the sample. Uncertainties are given as standard uncertainties.

<sup>d</sup>  $T_{\text{a}}$  is the temperature of the soap bubble meter used for measurement of the gas flow.

<sup>e</sup> Vapour pressure at temperature  $T$ , calculated from the  $m$  and the residual vapour pressure at the condensation temperature calculated by an iteration procedure.

<sup>f</sup> Standard uncertainties were calculated with  $u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa})$  for pressures from 5 to 3000 Pa. The standard uncertainties for  $T$ ,  $V$ ,  $p$ ,  $m$ , are standard uncertainties with 0.683 confidence level. Uncertainty of the vaporisation/sublimation enthalpy  $U(\Delta_{\text{l,cr}}^{\text{g}}H_{\text{m}}^{\circ})$  is the expanded uncertainty (0.95 level of confidence) calculated according to procedure described elsewhere [7,8]. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapour pressures, and uncertainties from adjustment of vaporisation enthalpies to the reference temperature  $T = 298.15 \text{ K}$ .

**Table S4**

The vapour pressures  $p$ , and standard vaporisation enthalpies and entropies obtained by the approximation of boiling points at different pressures available in the literature [9–11]

$T/$ K <sup>a</sup>	$p/$ Pa	$\Delta_1^g H_m^o/a$ kJ·mol <sup>-1</sup>	$\Delta_1^g S_m^o/$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
benzyl phenyl ether [946-80-5]			
$\Delta_1^g H_m^o(298.15 \text{ K}) = (74.7 \pm 2.4) \text{ kJ} \cdot \text{mol}^{-1}$			
$\Delta_1^g S_m^o(298.15 \text{ K}) = (146.3 \pm 2.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$			
$\Delta_1^g G_m^o(298.15 \text{ K}) = (31.0 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$			
$\ln(p/p_{\text{ref}}) = \frac{320.3}{R} - \frac{97982.6}{RT} - \frac{78.2}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$			
358	53	70.0	132.8
367	80	69.3	129.5
367	80	69.3	129.5
368	80	69.2	128.8
380	200	68.3	128.0
383	200	68.0	126.0
383	200	68.0	126.0
385	267	67.9	127.0
397	533	66.9	125.1
398	533	66.9	124.5
398	533	66.9	124.5
403	533	66.5	121.4
416	1200	65.5	120.6
425	2000	64.7	119.8
428	2000	64.5	118.2
433	2000	64.1	115.6
436	3200	63.9	117.9
437	3200	63.8	117.4
440	3200	63.6	115.9
451	4666	62.7	113.6
452	4666	62.6	113.1
559	101325	54.3	97.2
559	101325	54.3	97.2
560	101325	54.2	97.0
561	101325	54.1	96.6
dibenzyl ether [103-50-4]			
$\Delta_1^g H_m^o(298.15 \text{ K}) = (79.5 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$			
$\Delta_1^g S_m^o(298.15 \text{ K}) = (154.2 \pm 1.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$			
$\Delta_1^g G_m^o(298.15 \text{ K}) = (33.6 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$			
$\ln(p/p_{\text{ref}}) = \frac{336.4}{R} - \frac{105329.8}{RT} - \frac{86.5}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$			
365	40	73.8	137.0
367	40	73.6	135.4

367	40	73.6	135.4
367	40	73.6	135.4
368	53	73.5	137.1
368	53	73.5	137.1
381	107	72.4	133.1
382	107	72.3	132.3
398	267	70.9	128.9
399	267	70.9	128.5
400	333	70.8	129.7
400	333	70.8	129.7
403	400	70.5	129.0
403	400	70.5	129.0
407	400	70.2	126.7
407	400	70.1	126.4
413	667	69.6	126.9
421	800	68.9	123.5
423	933	68.8	123.9
425	933	68.6	122.8
427	1333	68.4	124.3
428	1333	68.3	123.7
430	1333	68.1	122.6
431	1200	68.1	121.4
431	1333	68.0	122.0
432	1333	68.0	121.4
433	1467	67.9	121.7
436	1733	67.6	121.4
437	2000	67.5	122.0
437	1733	67.5	120.8
437	1733	67.5	120.8
437	1867	67.5	121.4
438	1733	67.4	120.3
439	2000	67.4	120.9
439	2000	67.4	120.9
439	1867	67.4	120.3
443	2133	67.0	119.3
443	2133	67.0	119.3
445	2400	66.8	119.2
446	2800	66.8	119.9
447	2800	66.7	119.4
449	2666	66.5	118.0
457	4400	65.8	118.0
457	3733	65.8	116.6
471	7333	64.6	115.4
473	7333	64.4	114.5

571	101058	55.9	98.1
571	101325	55.9	98.1
571	101325	55.9	98.1

dicyclohexyl ether [4645-15-2];

$$\Delta_1^g H_m^o(298.15 \text{ K}) = (68.1 \pm 2.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^g S_m^o(298.15 \text{ K}) = (142.9 \pm 3.9) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^g G_m^o(298.15 \text{ K}) = (25.5 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{318.2}{R} - \frac{91834.4}{RT} - \frac{79.6}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

348	133	64.1	129.2
354	200	63.7	128.1
367	400	62.6	124.7
370	400	62.4	122.7
372	533	62.3	124.1
372	533	62.2	123.6
384	1733	61.3	125.8
387	1333	61.0	121.8
389	2000	60.9	124.1
392	2400	60.6	123.7
394	2400	60.5	122.5
404	4000	59.7	120.9
407	4000	59.4	119.3
511	98658	51.2	100.0
512	98658	51.1	99.7
512	96925	51.1	99.5
513	96925	51.0	99.2
515	101178	50.8	98.7
516	101325	50.8	98.5
517	101325	50.7	98.1

1,2-diphenyl-ethane [103-29-7];

$$\Delta_1^g H_m^o(298.15 \text{ K}) = (68.8 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^g S_m^o(298.15 \text{ K}) = (134.9 \pm 1.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^g G_m^o(298.15 \text{ K}) = (28.6 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{303.2}{R} - \frac{90415.3}{RT} - \frac{72.5}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

338	27	65.9	126.6
343	40	65.5	126.0
343	40	65.5	126.0
354	67	64.8	122.1
356	67	64.6	120.7
371	200	63.5	119.5
378	267	63.0	117.4
379	267	63.0	117.1
379	267	62.9	116.8
379	267	62.9	116.8

391	533	62.1	115.2
397	667	61.6	113.6
408	1067	60.8	111.4
408	1067	60.8	111.4
409	1333	60.8	112.7
410	1333	60.7	112.1
411	1467	60.6	112.4
412	1333	60.6	111.3
415	1600	60.3	111.0
421	2133	59.9	110.3
421	2000	59.9	109.7
443	5333	58.3	107.2
443	4666	58.3	106.1
557	101325	50.0	89.9
558	101325	50.0	89.7

1,2-dicyclohexyl-ethane [3321-50-4];

$$\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (68.2 \pm 2.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^{\text{g}}S_{\text{m}}^{\circ}(298.15 \text{ K}) = (137.1 \pm 2.6) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^{\text{g}}G_{\text{m}}^{\circ}(298.15 \text{ K}) = (27.3 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{314.8}{R} - \frac{92636.6}{RT} - \frac{82.0}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

348	80	64.1	125.3
359	133	63.2	121.0
366	240	62.6	120.9
371	267	62.2	118.4
389	667	60.8	114.8
391	800	60.6	114.8
400	1200	59.8	112.8
403	1333	59.6	112.0
403	1200	59.6	111.1
406	1800	59.3	112.8
407	1800	59.3	112.2
409	2000	59.1	112.0
413	2533	58.8	111.7
418	2666	58.4	109.5
423	2666	58.0	106.9
547	98125	47.8	87.3
547	101325	47.7	87.3

1,3-diphenyl-propane [1081-75-0];

$$\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (73.8 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^{\text{g}}S_{\text{m}}^{\circ}(298.15 \text{ K}) = (140.9 \pm 2.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^{\text{g}}G_{\text{m}}^{\circ}(298.15 \text{ K}) = (31.8 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{307.2}{R} - \frac{94830.3}{RT} - \frac{70.6}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

342	13	70.7	132.5
-----	----	------	-------

344	13	70.5	130.9
351	27	70.0	131.1
353	27	69.9	129.6
356	27	69.7	127.4
368	67	68.8	126.3
382	133	67.9	122.6
384	133	67.7	121.3
387	240	67.5	124.3
397	267	66.8	119.0
401	293	66.5	117.4
407	400	66.1	116.5
408	533	66.0	118.3
409	533	66.0	118.0
415	933	65.5	119.0
430	1867	64.5	116.8
430	1867	64.5	116.8
431	1867	64.4	116.3
439	2000	63.8	112.9
439	2133	63.8	113.4
441	2000	63.7	111.9
441	2133	63.7	112.4
571	101325	54.5	95.5
572	101325	54.5	95.4
573	101325	54.4	94.9
574	101325	54.3	94.7
576	101325	54.2	94.1

1,3-dicyclohexyl-propane [3178-24-3];

$$\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (72.9 \pm 3.0) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^{\text{g}}S_{\text{m}}^{\circ}(298.15 \text{ K}) = (144.1 \pm 1.7) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^{\text{g}}G_{\text{m}}^{\circ}(298.15 \text{ K}) = (29.9 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{328.4}{R} - \frac{99309.6}{RT} - \frac{88.6}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

382	267	65.5	122.1
383	267	65.4	121.4
434	3200	60.9	111.6
564	101325	49.3	87.6
565	101325	49.3	87.4
565	101325	49.3	87.3

dicyclohexylmethyl ether [14315-63-0];

$$\Delta_1^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (73.9 \pm 3.6) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_1^{\text{g}}S_{\text{m}}^{\circ}(298.15 \text{ K}) = (147.9 \pm 7.1) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_1^{\text{g}}G_{\text{m}}^{\circ}(298.15 \text{ K}) = (29.8 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln(p/p_{\text{ref}}) = \frac{343.0}{R} - \frac{103505.1}{RT} - \frac{99.4}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

356	53	68.1	128.7
-----	----	------	-------

368	133	66.9	126.8
369	133	66.8	126.1
426	3066	61.2	114.6
427	3066	61.1	114.0
574	101325	46.5	81.2
trans-2-methoxy-decalin [55473-38-6];			
$\Delta_1^g H_m^o(298.15 \text{ K}) = (58.7 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$			
$\Delta_1^g S_m^o(298.15 \text{ K}) = (123.8 \pm 5.7) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$			
$\Delta_1^g G_m^o(298.15 \text{ K}) = (21.8 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$			
$\ln(p/p_{\text{ref}}) = \frac{291.6}{R} - \frac{80151.0}{RT} - \frac{72.1}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$			
349	400	55.0	111.7
363	1067	54.0	110.9
364	1067	53.9	110.6
383	2000	52.5	104.6
383	2400	52.5	106.2
384	2000	52.5	104.1
509	101325	43.5	85.5

<sup>a</sup> Uncertainties in this table are expressed as the expanded uncertainty (0.95 level of confidence,  $k = 2$ ). Uncertainties of the vaporisation enthalpies include uncertainties from the fitting equation, and uncertainties from temperature adjustment to  $T = 298.15 \text{ K}$ . Uncertainties in the temperature adjustment of vaporisation enthalpies to the reference temperature  $T = 298.15 \text{ K}$  are estimated to account with 20 % to the total adjustment.

The vapour pressure-temperature dependencies were fitted by the following equation [5,6]:

$$R \cdot \ln(p_i/p_{\text{ref}}) = a + \frac{b}{T} + \Delta_1^g C_{p,m}^o \cdot \ln\left(\frac{T}{T_0}\right) \quad (\text{S2}),$$

where  $R = 8.314462 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  is the molar gas constant, the reference pressure  $p_{\text{ref}} = 1 \text{ Pa}$ ,  $a$  and  $b$  are adjustable parameters, the arbitrary temperature  $T_0$  applied in Eq. (S2) was chosen to be  $T_0 = 298.15 \text{ K}$  and  $\Delta_1^g C_{p,m}^o = C_{p,m}^o(\text{g}) - C_{p,m}^o(\text{liq})$  is the difference between the molar heat capacities of the gaseous  $C_{p,m}^o(\text{g})$  and the liquid phase  $C_{p,m}^o(\text{liq})$ , respectively. The  $\Delta_1^g C_{p,m}^o$ -values used in Eq. (S2) are given in Table S6.

### ***Adjustment of vaporisation enthalpies to the reference temperature $T = 298.18 \text{ K}$***

The standard molar enthalpies of vaporization at temperatures  $T$  were derived from the temperature dependence of the vapor pressures, approximated by Eq. (S2) using the following equation:

$$\Delta_{1,\text{cr}}^g H_m^o(T) = -b + \Delta_{1,\text{cr}}^g C_{p,m}^o \times T \quad (\text{S3})$$

where  $b$  is one of the adjustable parameters of Eq. (S2).

The  $\Delta_{1,\text{cr}}^g C_{p,m}^o$ -values used in Eq. (S3) are usually derived according to empirical equations developed by Acree and Chickos [12]:

$$\Delta_1^g C_{p,m}^o(298.15 \text{ K}) = -0.26 \times C_{p,m}^o(\text{liq}, 298.15 \text{ K}) - 10.58 \quad (\text{S4})$$

$$\Delta_{\text{cr}}^g C_{p,m}^o(298.15 \text{ K}) = -0.15 \times C_{p,m}^o(\text{cr}, 298.15 \text{ K}) - 0.75 \quad (\text{S5})$$

where  $C_{p,m}^o(\text{cr}, 298.15 \text{ K})$  or  $C_{p,m}^o(\text{liq}, 298.15 \text{ K})$  values are of experimental origin or they can be also estimated according to the group-additivity procedure by Chickos *et al.* [13]. The empirical coefficients in Eqs. (S4) and (S5) were originally derived from experimental data available for various organic compounds, but very few aromatic ethers participated in the parameterization of these equations.

The vapor pressures of the solid benzyl phenyl ether and 2-methoxy-naphthalene were measured in this work possibly close to the reference temperature  $T = 298.15 \text{ K}$  (see Table S2). Therefore, according to Eq. (3) derived enthalpies of vaporization at  $T = 298.15 \text{ K}$  cannot be significantly influenced by the inaccuracy of the differences in the isobaric heat capacities,  $\Delta_{\text{cr}}^g C_{p,m}^o$ . In contrast, the vapor pressures available in the literature over the liquid phase of aromatic ethers and hydrocarbons were mostly measured at higher temperatures and even at temperatures close to the boiling point. For this type of vapor pressure data, the influence of differences in isobaric heat capacities  $\Delta_1^g C_{p,m}^o$  is significant.

The validity of the  $\Delta_1^g C_{p,m}^o$ -values can be independently checked with help of the Clarke and Glew equation [14]:

$$R \times \ln(p_i/p^o) = -\frac{\Delta_1^g G_m^o(\theta)}{\theta} + \Delta_1^g H_m^o(\theta) \left(\frac{1}{\theta} - \frac{1}{T}\right) - \Delta_1^g C_{p,m}^o(\theta) \left(\frac{\theta}{T} - 1 + \ln\left(\frac{T}{\theta}\right)\right) \quad (\text{S6}),$$

where  $p_i$  is the vapour pressure at the temperature  $T$ ,  $p^o$  is an arbitrary reference pressure ( $p^o = 1 \text{ Pa}$  in this work),  $\theta$  is an arbitrary reference temperature (in this work we use  $\theta = 298.15 \text{ K}$ ),  $R$  is the molar gas constant,  $\Delta_1^g G_m^o(\theta)$  is the difference in the standard molar Gibbs energy between the gaseous and the liquid phases,  $\Delta_1^g H_m^o(\theta)$  is the standard molar vaporization enthalpy, and  $\Delta_1^g C_{p,m}^o(\theta)$  is the difference in the molar heat capacity at constant pressure between the gaseous and the liquid phase. An advantage of the Clarke and Glew equation is that the fitting coefficients (in contrast to Eq. (S2)) are directly related to the thermodynamic functions of vaporization. In our experience, however, a prerequisite for the application of Clarke and Glew's equation is good quality and consistency of the experimental data. In addition, the vapour pressures used for the fitting should cover the temperature range of at least 100 K. The available reliable experimental vapour pressures for aliphatic and aromatic ethers were approximated using Eq. (S6) and the  $\Delta_1^g C_{p,m}^o$ -values were derived and analyzed. It has turned out that the  $\Delta_1^g C_{p,m}^o$ -values calculated using the conventional method of Acree and Chickos [12] are systematically and significantly overestimated when the procedure is applied to ethers. This observation has prompted the re-calculations of the empirical coefficients in Eq. (S4) using the  $\Delta_1^g C_{p,m}^o$ -values evaluated according to Eq. (S6) from reliable vapor pressures. With the results from [15,16], the specific for ether equations were derived:

$$\text{aromatic ethers} \quad \Delta_1^g C_{p,m}^o(298.15 \text{ K}) = -0.26 \times C_{p,m}^o(\text{liq}, 298.15 \text{ K}) + 2.0 \quad (\text{S7}),$$

$$\text{aliphatic ethers} \quad \Delta_1^g C_{p,m}^o(298.15 \text{ K}) = -0.31 \times C_{p,m}^o(\text{liq}, 298.15 \text{ K}) + 17.4 \quad (\text{S8}),$$

and used in this work for the temperature adjustments of vaporization enthalpies of aromatic and cyclic ethers to the reference temperature  $T = 298.15 \text{ K}$  (see Tables S2-S3).

The similar specific equations were derived for alkyl-cyclohexanes [17]:

$$\Delta_1^g C_{p,m}^o(298.15 \text{ K}) = -0.8 \times \Delta_1^g C_{p,m}^o(298.15 \text{ K from Eq. S4}) \quad (\text{S9}),$$

as well as for alkyl-biphenyl and related compounds [18]:

$$\Delta_1^g C_{p,m}^o(298.15 \text{ K}) = -0.26 \times C_{p,m}^o(\text{liq}, 298.15 \text{ K}) + 18.9 \quad (\text{S10}),$$

These equation were used in this work for the temperature adjustments of vaporization enthalpies of alkyl-cyclohexanes, 1,2-diphenyl-ethane and 1,3-diphenyl-propane to the reference temperature  $T = 298.15 \text{ K}$  (see Table S3).

The standard molar vaporization entropies at temperatures  $T$  were also derived from the temperature dependences of the vapor pressures (approximated by Eq. S1) as follows:

$$\Delta_{i,\text{cr}}^g S_m^o(T) = \Delta_{i,\text{cr}}^g H_m^o/T + R \times \ln(p_i/p^o) \quad (\text{S11})$$

with  $p^o = 0.1 \text{ MPa}$ .

### *Differential scanning calorimetry: thermal behavior and fusion enthalpies*

The thermal behavior of crystalline sample of benzyl phenyl ether including melting temperature  $T_{\text{fus}}$ , and the standard molar enthalpy of fusion,  $\Delta_{\text{cr}}^l H_m^o(T_{\text{fus}})$ , was studied with a commercial DSC Mettler Toledo DSC 822e coupled with Huber TC100MT cooler. The sample was placed in the standard non-pinned aluminium pan of 40  $\mu\text{l}$  volume. The pan and sample were weighed with the Sartorius MSE3.6P-000-DM microbalance with the standard uncertainty of  $5 \cdot 10^{-6} \text{ g}$ . The calibration of the DSC was checked with melting behaviour of reference indium sample. The twice standard deviation of the enthalpy of fusion in the test measurements for reference compound was  $\pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\pm 0.3 \text{ K}$  for the melting temperature. Uncertainties of the enthalpy of fusion values are expressed as expanded uncertainties (at a level of confidence of 0.95,  $k=2$ ). They include uncertainties from fusion experiment and calibration. Details are reported elsewhere [19].

In the first DSC run the sample was heated with a rate  $10 \text{ K}\cdot\text{min}^{-1}$  to  $378 \text{ K}$  ( $\sim 20 \text{ K}$  above melting temperature provided by supplier) and then cooled down to  $298 \text{ K}$  also with the rate  $10 \text{ K}\cdot\text{min}^{-1}$ . Such procedure provided sufficient contact between the sample and the bottom of pan. The DSC experiments were repeated three times with the average result is given in Table S5.

**Table S5**

Enthalpies of fusion ( $\Delta_{\text{cr}}^l H_m^o$ ), vaporization ( $\Delta_1^g H_m^o$ ) and sublimation ( $\Delta_{\text{cr}}^g H_m^o$ ) at melting points ( $T_{\text{fus}}$ ) and at  $298.15 \text{ K}$  of benzyl phenyl ether and 2-methoxy-naphthalene<sup>a</sup>

	$T_{\text{fus}}$	$\Delta_{\text{cr}}^l H_m^o(T_{\text{fus}})$	$\Delta_{\text{cr}}^l H_m^o(298 \text{ K})^b$	$\Delta_{\text{cr}}^g H_m^o(298 \text{ K})$	$\Delta_1^g H_m^o(298 \text{ K})$
Compound	K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
benzyl phenyl ether [this work]	$311.4 \pm 0.2$	$22.2 \pm 0.3$	$21.6 \pm 0.4$	$95.3 \pm 0.6^c$	$73.7 \pm 0.5^d$
2-methoxynaphthalene	$346.3 \pm 0.2$ [20]	$22.5 \pm 0.4$ [20]	$21.2 \pm 0.6$	$90.4 \pm 0.5$ [Table S2]	$69.2 \pm 0.8^e$

<sup>a</sup> Uncertainties are presented as expanded uncertainties (0.95 level of confidence with  $k=2$ ).

<sup>b</sup> The experimental enthalpy of fusion  $\Delta_{\text{cr}}^1 H_m^{\text{o}}$  measured at  $T_{\text{fus}}$  was adjusted to 298.15 K according to procedure developed by Acree and Chickos [12]:

$$\Delta_{\text{cr}}^1 H_m^{\text{o}}(298.15 \text{ K})/(\text{J}\cdot\text{mol}^{-1}) = \Delta_{\text{cr}}^1 H_m^{\text{o}}(T_{\text{fus}}/\text{K}) - (\Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\text{o}} - \Delta_1^{\text{g}} C_{p,m}^{\text{o}}) \times [(T_{\text{fus}}/\text{K}) - 298.15 \text{ K}]$$

where  $\Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\text{o}}$  and  $\Delta_1^{\text{g}} C_{p,m}^{\text{o}}$  were taken from Table S5. Uncertainties in the temperature adjustment of fusion enthalpies from  $T_{\text{fus}}$  to the reference temperature are estimated to account with 30 % to the total adjustment [12].

<sup>c</sup> The sum of columns 4 and 6 in this table.

<sup>d</sup> The enthalpy of vaporisation evaluated in Table 2 (main text).

<sup>e</sup> Calculated as the difference between columns 5 and 4 in this table.

The uncertainties of the melting temperature and the enthalpy of fusion are expressed as an expanded uncertainties with a confidence level of 95 % ( $k \approx 2$ ). The melting temperature was evaluated as the onset temperature of the melting peak adjusted to the zero heating rate. The purity of the sample as determined from the slope of the corrected linear data on the Van't Hoff plot was  $99.81 \pm 0.06\%$ .

As a rule, thermochemical calculations are commonly performed at the reference temperature  $T = 298.15 \text{ K}$ . The adjustment of  $\Delta_{\text{cr}}^1 H_m^{\text{o}}(T_{\text{fus}})$  was performed with help of the equation [S12]:

$$\Delta_{\text{cr}}^1 H_m^{\text{o}}(298.15 \text{ K})/(\text{J}\cdot\text{mol}^{-1}) = \Delta_{\text{cr}}^1 H_m^{\text{o}}(T_{\text{fus}}/\text{K}) - (\Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\text{o}} - \Delta_1^{\text{g}} C_{p,m}^{\text{o}}) \times [(T_{\text{fus}}/\text{K}) - 298.15 \text{ K}] \quad (\text{S12})$$

where  $\Delta_{\text{cr}}^{\text{g}} C_{p,m}^{\text{o}}$  and  $\Delta_1^{\text{g}} C_{p,m}^{\text{o}}$  were taken from Table S6. With this adjustment, the molar enthalpies of fusion,  $\Delta_{\text{cr}}^1 H_m^{\text{o}}(298.15 \text{ K})$  were calculated. Uncertainties in the temperature adjustment of fusion enthalpy from  $T_{\text{fus}}$  to the reference temperature were estimated to account with 30 % to the total adjustment [12].

**Table S6**

Compilation of data on molar heat capacities  $C_{p,m}^{\text{o}}(\text{liq})$  and heat capacity differences  $\Delta_1^{\text{g}} C_{p,m}^{\text{o}}$  (in  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) at  $T = 298.15 \text{ K}$

Compounds	$C_{p,m}^{\text{o}}(\text{liq})^{\text{a}}$	$-\Delta_1^{\text{g}} C_{p,m}^{\text{o}}^{\text{b}}$
benzene	136.4 [21]	
cyclohexane	156.3 [22]	
methoxy-benzene	199.0 [16]	
methoxy-cyclohexane	203.0	45.5 [Eq. 8]
diphenyl-methane	266.1 [21]	
dicyclohexyl-methane	321.7	
diphenyl-ether	267.5 [23]	
dicyclohexyl ether	313.0	79.6 [Eq. 8]
1,2-diphenyl-ethane	312.4	72.5 <sup>c</sup>
1,2-dicyclohexyl-ethane	353.6	82.0 [Eq. 9]
benzyl phenyl ether <sup>d</sup>	308.5	78.2 [Eq. 7]
cyclohexylmethoxy-cyclohexane	344.9	89.5 [Eq. 8]
1,3-diphenyl-propane	344.3	70.6 [Eq. 10]
1,3-dicyclohexyl-propane	385.5	88.6 [Eq. 9]
dibenzyl ether	340.4	86.5 [Eq. 7]
dicyclohexylmethyl ether	376.8	99.4 [Eq. 8]
naphthalene	205.0	

trans-decalin	232.0 [24]	
2-methoxy-naphthalene	261.4	
trans-2-methoxy-decalin	288.8	72.1 [Eq. 8]

<sup>a</sup> Calculated according to the group-additivity procedure developed by Acree and Chickos [12].

<sup>b</sup> Calculated according to the empirical procedures developed by Acree and Chickos [12] and modified in this work (see text above).

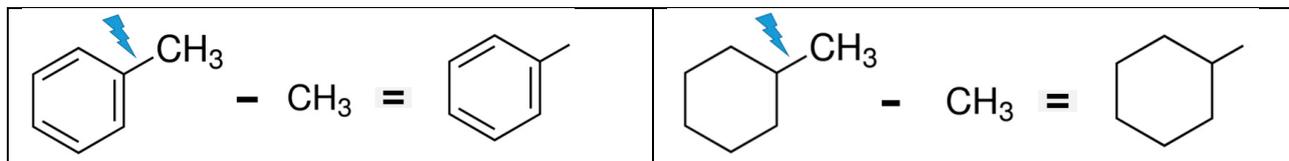
<sup>c</sup> From Table S7.

<sup>d</sup> For the crystalline sample  $C_{p,m}^o(\text{cr}) = 237.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $\Delta_{\text{cr}}^{\text{g}}C_{p,m}^o = 36.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  calculated according to the procedure developed by Acree and Chickos [12].

**Table S7.** Coefficients of the Clarke and Glew equation (S6) for 1,2-diphenyl-ethane from Osborn et al. [25]<sup>a</sup>

$T$ -range	$\Delta_1^{\text{g}}G_m^o(298.15 \text{ K})$	$\Delta_1^{\text{g}}H_m^o(298.15 \text{ K})$	$-\Delta_1^{\text{g}}C_{p,m}^o(298.15 \text{ K})$
K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
333.2-413.2	$28.6\pm 0.1$	$69.2\pm 0.1$	$72.5\pm 1.1$

<sup>a</sup>Uncertainties of thermodynamic functions are expressed as the standard uncertainty.



**Figure S1** The development of the contributions C<sub>6</sub>H<sub>5</sub>- (left) and C<sub>6</sub>H<sub>11</sub>- (right) for calculating the vaporization enthalpies (or gas-phase enthalpies of formation) of aromatic and cyclic aliphatic hydrocarbons using the GA method. All values in  $\text{kJ}\cdot\text{mol}^{-1}$ . The numerical values of the contributions are given in Table S8. Results of calculations are shown in Table S9.

**Table S8**

Group-additivity values  $i$  for calculation of enthalpies of vaporization,  $\Delta_1^{\text{g}}H_m^o$ , and enthalpies of formation,  $\Delta_f H_m^o(\text{g})$ , of alkanes, ethers, and aromatics at 298.15 K in  $\text{kJ mol}^{-1}$

	$\Delta_1^{\text{g}}H_m^o$	$\Delta_f H_m^o(\text{g})$
	$i$ [26]	$i$ [26]
<b>Alkanes</b>		
C-(C)(H) <sub>3</sub>	6.33	-41.80
C-(C) <sub>2</sub> (H) <sub>2</sub>	4.52	-23.06
C-(C) <sub>3</sub> (H)	1.24	-10.49
C-(C) <sub>4</sub>	-2.69	-3.17
C <sub>6</sub> H <sub>11</sub> -	29.1	-113.0
<b>Ethers</b>		

O-(C) <sub>2</sub>	6.80	-100.7
C-(O)(H) <sub>3</sub>	6.33	-41.80
C-(O)(C)(H) <sub>2</sub>	3.9	-34.87
C-(O)(C) <sub>2</sub> (H)	1.0	-31.15
C-(O)(C) <sub>3</sub>	-2.43	-25.01
<b>Aromatics</b>		
C <sub>b</sub> -(C <sub>b</sub> ) <sub>2</sub> (H)	5.65	13.77
C <sub>b</sub> -(C <sub>b</sub> ) <sub>2</sub>	3.44	22.81
C-(O)(C <sub>b</sub> )(H) <sub>2</sub>	3.9	-28.1
C <sub>6</sub> H <sub>5</sub> -	31.8	91.9
C <sub>6</sub> H <sub>5</sub> -O-	40.1	-28.9

<sup>a</sup> C<sub>b</sub> is the carbon atom in the benzene ring.

**Table S9**

Comparison of experimental thermochemical data with those calculated by group additivity at  $T = 298.15$  K ( $p^\circ = 0.1$  MPa) for ethers and hydrocarbons (in  $\text{kJ}\cdot\text{mol}^{-1}$ )<sup>a</sup>

compound	$\Delta_f^\circ H_m^\circ(\text{GA})^a$	$\Delta_f^\circ H_m^\circ(\text{exp})^b$	$\Delta_f H_m^\circ(\text{g})_{\text{GA}}^a$	$\Delta_f H_m^\circ(\text{g})_{\text{exp}}^b$
phenyl benzyl ether	75.8±1.5	73.7±0.5	34.9±4.0	30.6±3.1
cyclohexylmethoxy-cyclohexane	69.7±1.5	-	-376.8±4.0	-372.0±4.1
dibenzyl ether	78.2±1.5	78.5±0.5	26.9±4.0	28.5±3.0
dicyclohexylmethyl ether	72.8±1.5	73.0±1.4	-396.5±4.0	-386.8±4.1
1,2-diphenyl-ethane	71.2±1.5	69.1±0.9	145.4±4.0	133.7±4.1
1,2-dicyclohexyl-ethane	67.2±1.5	67.6±1.1	-272.2±4.0	-261.0±4.1
1,3-diphenyl-propane	75.7±1.5	73.3±1.3	122.3±4.0	114.7±4.1
1,3-dicyclohexyl-propane	71.8±1.5	71.8±1.1	-295.3±4.0	-281.6±4.1

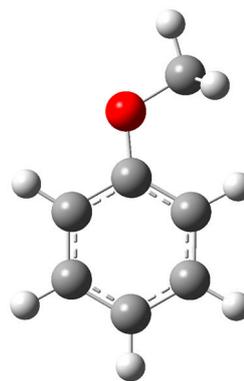
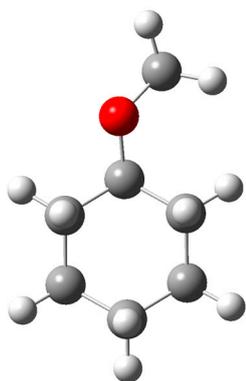
<sup>a</sup> Calculated with group contributions from Table S8.

<sup>b</sup> From Table 5.

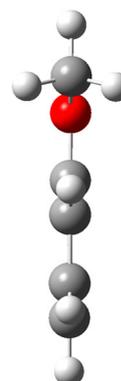
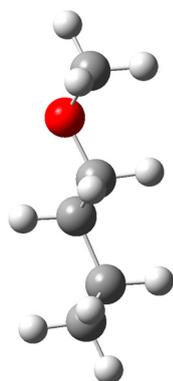
# Quantum-chemical calculations

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Front view



Side view

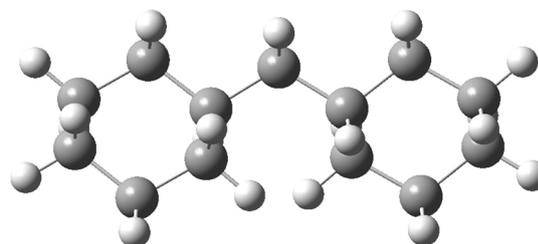
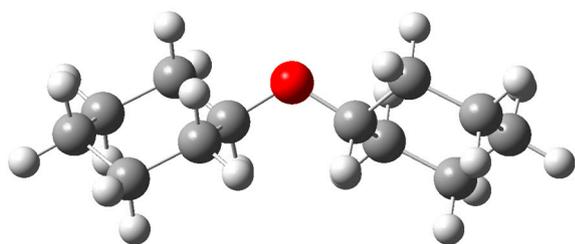


methoxy-cyclohexane

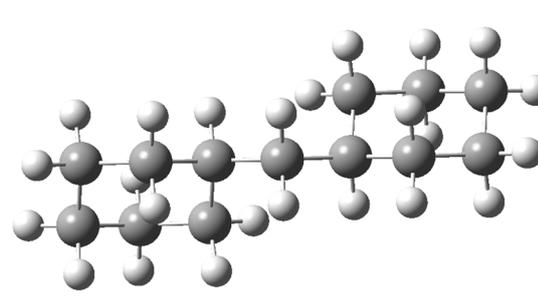
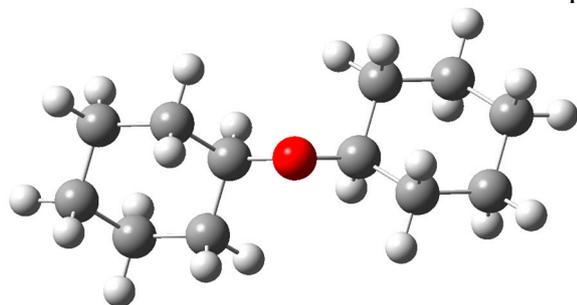
methoxy-benzene

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Front view



Top view

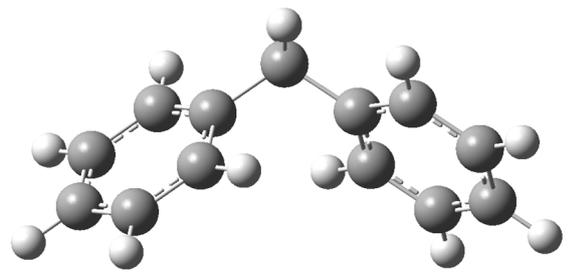
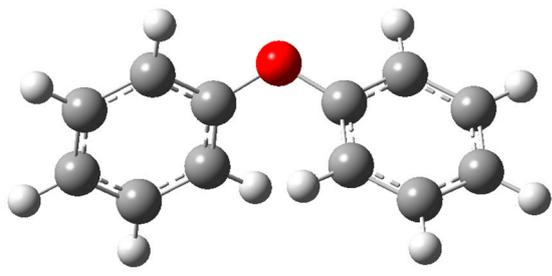


dicyclohexyl ether

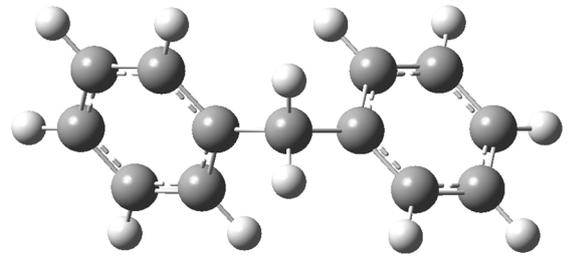
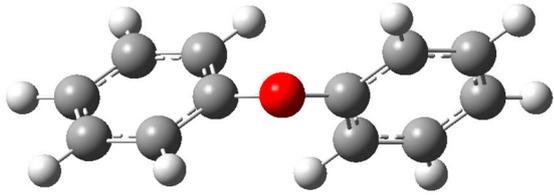
dicyclohexyl-methane

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Front view



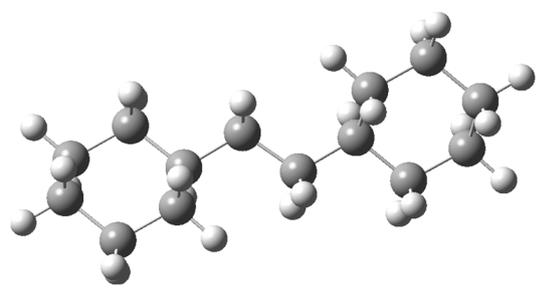
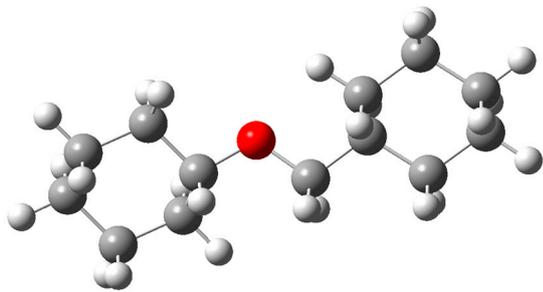
Top view



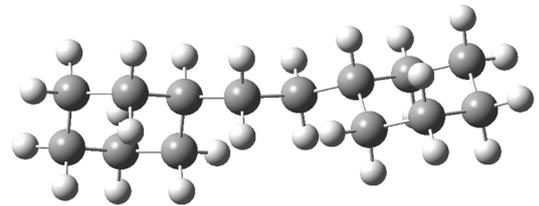
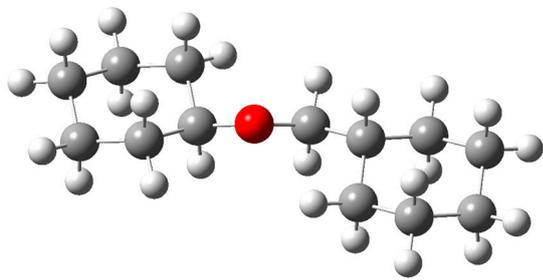
diphenyl-ether

diphenyl-methane

Front view



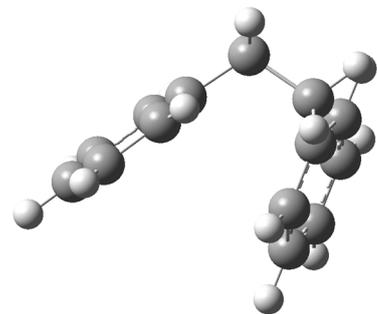
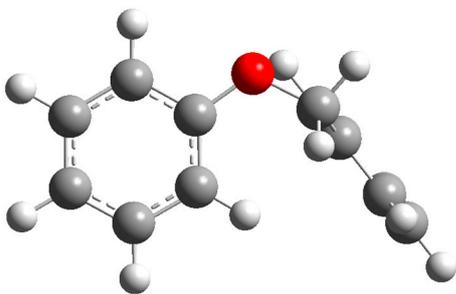
Top view



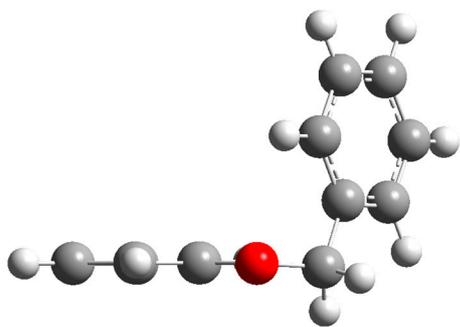
cyclohexylmethoxy-cyclohexane

1,2-dicyclohexyl-ethane

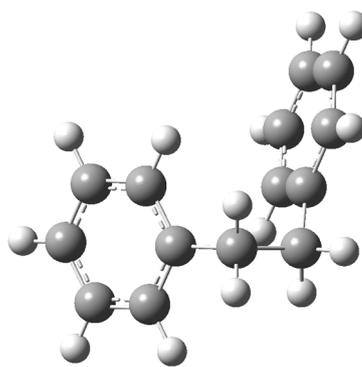
Front view



Top view



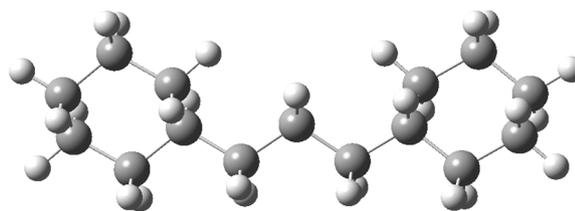
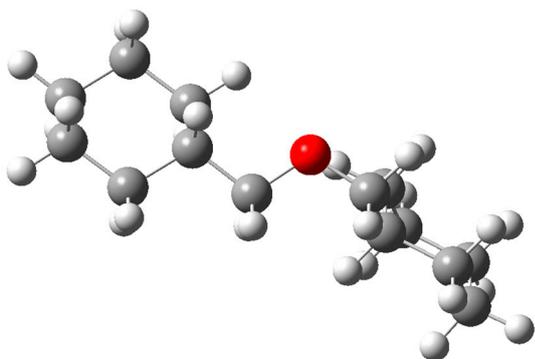
benzyl phenyl ether



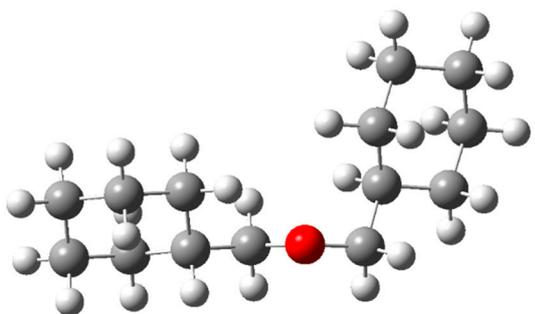
1,2-diphenyl-ethane

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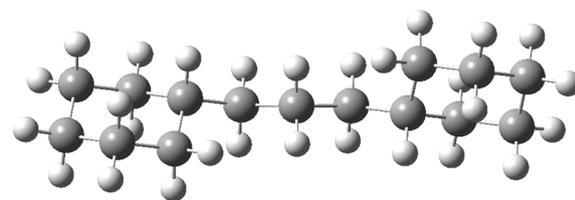
Front view



Top view



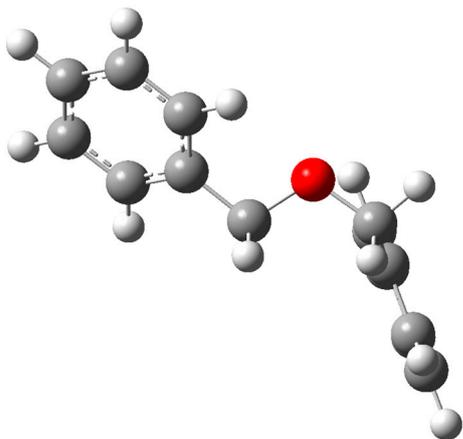
dicyclohexylmethyl ether



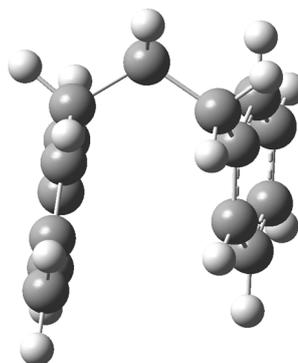
1,3-dicyclohexyl-propane

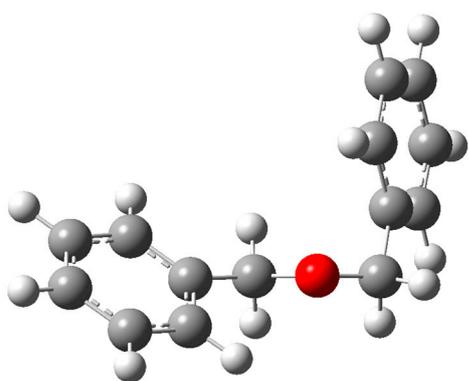
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Front view

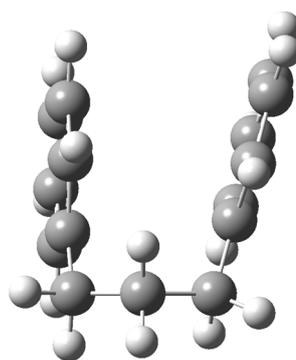


Top view



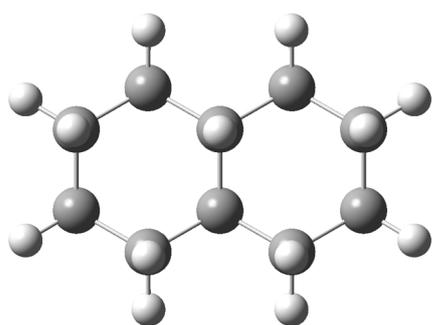


dibenzyl ether

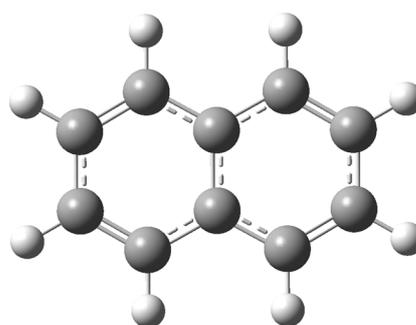


1,3-diphenylpropane

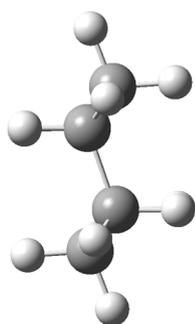
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Front view



Side view

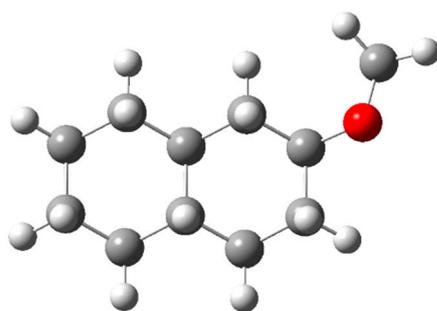


trans-decalin

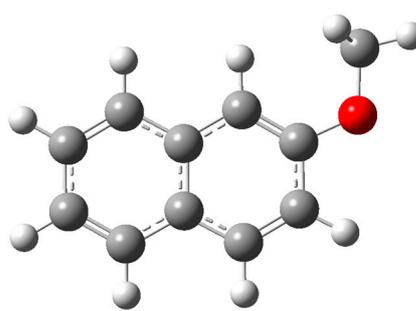


naphthalene

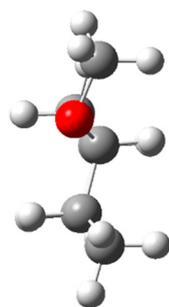
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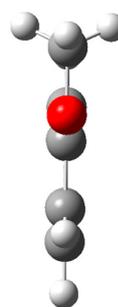
Front view



Side view



trans-2-methoxy-decalin



2-methoxy-naphthalene

**Figure S2** The most stable conformers for the aromatic compounds and their perhydrogenated products.

**Table S10**

Calculation of the G3MP2 *corrected* gas-phase enthalpies at  $T = 298.15$  K (in  $\text{kJ}\cdot\text{mol}^{-1}$ )

	$\Delta_f H_m^\circ(\text{g})_{\text{exp}}$	$\Delta_f H_m^\circ(\text{g})_{\text{AT}}$	$\Delta_f H_m^\circ(\text{g})_{\text{AT}}^{\text{a}}$ (corr)	<sup>b</sup>
biphenyl	179.7±1.1 [27]	165.0	176.5	3.2
2-methyl-biphenyl	152.3±2.3 [28]	136.3	149.0	3.3
4-methyl-biphenyl	141.4±2.1 [28]	132.5	145.4	-4.0
2,2'-dimethyl-biphenyl	117.3±2.6 [28]	101.5	115.7	1.6
3,3'-dimethyl-biphenyl	107.9±2.7 [28]	96.4	110.8	-2.9
4,4'-di-methyl-biphenyl	110.8±3.2 [28]	100.0	114.3	-3.5
2-ethyl-biphenyl	127.6±2.7 [18]	114.0	127.7	-0.1
3-iso-propyl-biphenyl	96.7±3.5 [18]	82.3	97.3	-0.6
4-tert-butyl-biphenyl	73.0±2.5 [18]	54.9	71.1	1.9
4,4'-di-tert-butyl-biphenyl	-33.7±3.4 [18]	-55.4	-34.6	0.9
1,2-diphenylethane; 103-29-7		120.3	<b>133.7</b>	
1,3-diphenylpropane; 1081-75-0		100.5	<b>114.7</b>	

<sup>a</sup> Calculated according to equation:

$$\Delta_f H_m^\circ(\text{g})_{\text{QC}} / \text{kJ}\cdot\text{mol}^{-1} = 0.9576 \times \Delta_f H_m^\circ(\text{g}, \text{AT})_{\text{G3MP2}} + 18.5 \quad \text{with } R^2 = 0.9979$$

Uncertainties are assessed to be  $\pm 4.1$   $\text{kJ}\cdot\text{mol}^{-1}$  (0.95 level of confidence with  $k=2$ ).

<sup>b</sup> Difference between experimental and calculated values

**Table S11**

Comparison of experimental and G3MP2 calculated gas-phase enthalpies of formation for alkyl-cyclohexanes (at  $T = 298.15$  K,  $p^\circ = 0.1$  MPa, in  $\text{kJ}\cdot\text{mol}^{-1}$ ) from [17].

compound	$\Delta_f H_m^\circ(\text{g}, AT)_{\text{G3MP2}}^a$	$\Delta_f H_m^\circ(\text{g})_{\text{exp}}^b$	$\Delta_f H_m^\circ(\text{g})_{\text{theor}}^c$	<sup>d</sup>
cyclohexane	-122.6	-123.4±0.8	-122.1	-1.3
Me-cyclohexane	-154.7	-154.7±1.0	-153.3	-1.4
trans-1,2-di-Me-cyclohexane	-182.8	-179.9±1.9	-180.5	0.6
cis-1,2-di-Me-cyclohexane	-175.9	-172.1±1.8	-173.8	1.7
trans-1,3-di-Me-cyclohexane	-179.3	-176.5±1.7	-177.1	0.6
cis-1,3-di-Me-cyclohexane	-186.7	-184.6±1.8	-184.3	-0.3
trans-1,4-di-Me-cyclohexane	-186.6	-184.5±1.8	-184.2	-0.3
cis-1,4-di-Me-cyclohexane	-179.4	-176.6±1.8	-177.2	0.6
Et-cyclohexane	-173.8	-171.7±1.6	-171.8	0.1
n-Pr-cyclohexane	-195.3	-192.5±1.0	-192.6	0.1
n-Bu-cyclohexane	-216.8	-213.3±1.3	-213.5	0.2
n-Dec-cyclohexane	-344.9	-339.5±2.5	-337.8	-1.7
n-Dodec-cyclohexane	-387.6	-378.7±3.7	-379.2	0.5
trans-1,4-di-tBu-cyclohexane	-330.5	-323.2±2.4	-323.8	0.6
1,2-dicyclohexylethane; 3321-50-4	-265.8		<b>-261.0</b>	
1,3-dicyclohexylpropane; 3178-24-3	-287.0		<b>-281.6</b>	

<sup>a</sup> Calculated by G3MP2 and atomization reaction.

<sup>b</sup> From Pedley *et al.* [29]. Uncertainties in this table are expressed as two times the standard deviation. The values given in brackets appear to be in error.

<sup>c</sup> Calculated according to equation:

$$\Delta_f H_m^\circ(\text{g})_{\text{theor}} / \text{kJ}\cdot\text{mol}^{-1} = 0.970 \times \Delta_f H_m^\circ(\text{g}, AT)_{\text{G3MP2}} - 3.2 \quad \text{with } R^2 = 0.9998$$

<sup>d</sup> Difference between column 3 and column 4.

**Table S12**

Thermochemical data at  $T = 298.15$  K ( $p^\circ = 0.1$  MPa) for auxiliary compounds (in  $\text{kJ}\cdot\text{mol}^{-1}$ )

Compounds	$\Delta_f H_m^\circ(\text{liq})$	$\Delta_f^\xi H_m^\circ$	$\Delta_f H_m^\circ(\text{g})$
benzene [30]	49.0±0.9	33.9±0.1	82.9±0.9
methoxy-benzene [31]	-116.9±0.7	46.4±0.2	-70.3±0.7
cyclohexane [29]	-156.4±0.8	33.1±0.2	-123.4±0.8
methoxy-cyclohexane [32]	-313.7±3.5	43.0±0.5	-270.7±3.5
toluene [30]	12.0±1.1	38.1±0.1	50.1±1.1
methyl-cyclohexane [29]	-190.1±1.0	35.4±0.2	-154.7±1.0
naphthalene [30]	95.2±2.1	55.4±1.4	150.6±1.5
trans-decalin [29]	-230.6±1.0	48.6±0.2	-182.0±1.0

### ***Gibbs energies of hydrogenation and transfer hydrogenation reactions***

As a rule, the thermodynamic calculations are initially carried out at the reference temperature  $T = 298$  K. Using the standard molar isobaric heat capacities  $C_{p,m}^{\circ}$  of reaction participants, the feasibility of the reaction at any desired temperature can be derived with the aid of Kirchhoff's law. The variation of reaction enthalpies and entropies with temperature is given by the thermodynamic relations

$$\Delta_r H_m^{\circ}(\text{liq}, T) = \Delta_r H_m^{\circ}(\text{liq}, 298.15 \text{ K}) + \Delta_r C_{p,m}^{\circ}(\text{liq}) \times (T - 298.15 \text{ K}) \quad (\text{S13})$$

$$\Delta_r S_m^{\circ}(\text{liq}, T) = \Delta_r S_m^{\circ}(\text{liq}, 298.15 \text{ K}) + \Delta_r C_{p,m}^{\circ}(\text{liq}) \times \ln(T/298.15 \text{ K})$$

(S14)

where  $\Delta_r C_{p,m}^{\circ}(\text{liq})$  is the change in standard molar heat capacity for the reaction, which is calculated analogously to Hess's Law from the standard molar heat capacities,  $C_{p,m}^{\circ}(\text{liq})$ , of reactants and products (see Table S6). The latter values are also functions of temperatures, which are not readily available for the diversity of the LOHC structures and their hydrogenated counterparts. However, if the  $C_{p,m}^{\circ}(\text{liq})$ -values for individual species can be large and change greatly over temperature intervals of  $(T - 298.15 \text{ K})$ , the  $\Delta_r C_{p,m}^{\circ}$ -values for reactions tend to be small and change little over such intervals. This observation applies in particular to the reactions shown in Fig. 1, as the structures of the reactants on the left and right sides of the reactions differ only slightly during hydrogenation. Therefore, in this work the  $\Delta_r C_{p,m}^{\circ}$ -values at 298.15 K were used for adjustment of  $\Delta_r H_m^{\circ}(\text{liq}, T)$  and  $\Delta_r S_m^{\circ}(\text{liq}, T)$  to  $T = 400$  K and  $T = 500$  K, as well as calculation of  $\Delta_r G_m^{\circ}(400 \text{ K})$  and  $\Delta_r G_m^{\circ}(500 \text{ K})$ , which are shown in Table S13 (last columns)

**Table S13.** Liquid phase thermodynamic properties of the hydrogenation of the hydrogen-lean LOHC counterparts

reactants	$\Delta_r H_m^\circ$ <sup>a</sup> (298 K) kJ·mol <sup>-1</sup>	$S_m^\circ$ <sup>b</sup> (298 K) J·mol <sup>-1</sup> ·K <sup>-1</sup>	$C_{p,m}^\circ$ <sup>c</sup> (298 K) J·mol <sup>-1</sup> ·K <sup>-1</sup>	$\Delta_r H_m^\circ$ <sup>d</sup> (298 K) kJ·mol <sup>-1</sup>	$\Delta_r S_m^\circ$ <sup>e</sup> (298 K) J·mol <sup>-1</sup> ·K <sup>-1</sup>	$\Delta_r C_{p,m}^\circ$ <sup>f</sup> (298 K) J·mol <sup>-1</sup> ·K <sup>-1</sup>	$\Delta_r G_m^\circ$ <sup>g</sup> (298 K) kJ·mol <sup>-1</sup>	$\Delta_r G_m^\circ$ <sup>h</sup> (400 K) kJ·mol <sup>-1</sup>	$\Delta_r G_m^\circ$ <sup>h</sup> (500 K) kJ·mol <sup>-1</sup>
benzene	49.0	173.3	136.4						
cyclohexane	-156.4	204.3	156.3						
				-205.4	-360.9	-66.5	-97.8	-60.1	-21.1
				-68.5	-120.3		-32.6	-20.0	-7.0
methoxy-benzene	-116.9	234.8	199.0						
methoxy-cyclohexane	-313.7	270.1	203.0						
				-197.7	-356.7	-82.4	-91.3	-23.9	-14.6
				-65.9	-118.9		-30.4	-18.0	4.9
diphenyl-methane	96.6	299.8	266.1						
dicyclohexyl-methane	-307.1	334.2	321.7						
				-403.7	-749.7	-117.2	-180.2	-102.2	-22.1
				-67.3	-125.0		-30.0	-17.0	-3.7
diphenyl-ether	-15.8	305.3	267.5						
dicyclohexyl ether	-424.3	332.2	313.0						
				-408.5	-757.2	-127.3	-182.7	-103.8	-22.5
				-68.1	-126.2		-30.5	-17.3	-3.8
1,2-diphenyl-ethane	64.6	331.5	312.4						
1,2-dicyclohexyl-ethane	-328.6	373.4	353.6						
				393.2	-742.2	-131.6	-171.9	-94.5	-14.5
				-65.5	-123.7		-28.7	-15.7	-2.4
benzyl phenyl ether	-43.1	314.7	308.5						
cyclohexylmethoxy-cyclohexane	-441.7	366.1	344.9						
				-398.6	-732.7	-136.4	-180.2	-103.6	-24.3
				-66.4	-122.1		-30.0	-17.3	-4.1
1,3-diphenyl-propane	41.4	358.0	344.3						
1,3-dicyclohexyl-propane	-353.4	400.3	385.5						
				-394.8	-741.8	-131.6	-173.6	-96.2	-16.3
				-65.8	-123.6		-28.9	-16.0	-2.7
dibenzyl ether	-50.0	350.6	340.4						
dicyclohexylmethyl ether	-459.8	391.3	376.8						
				-409.8	-743.4	-136.4	-188.2	-110.5	-30.2
				-68.3	-123.9		-31.4	-18.4	-5.0
naphthalene	94.9	217.6	205.0						
trans-decalin	-230.6	264.9	232.0						
				-325.5	-606.1	-117.0	-144.8	-81.4	-15.7
				-65.1	-121.2		-29.0	-16.3	-3.1
2-methoxy-naphthalene	-75.9	263.6	261.4						
trans-2-methoxy-decalin	-388.1	322.5	288.8						
				-312.2	-594.5	-116.6	-134.9	-72.8	-8.2
				-62.4	-118.9		-27.0	-14.6	-1.6

<sup>a</sup> From Table 5.

<sup>b</sup> From Table 7.

<sup>c</sup> From Table S6.

<sup>d</sup> Calculated according to Eq. (11) from standard molar enthalpies of formation of reactants from Table 3.

<sup>e</sup> Calculated according to Eq. (12) from standard molar entropies of reactants from Table 2.

<sup>f</sup> The difference in the standard molar heat capacities of reactants calculated from data given in Table S6.

<sup>g</sup> Calculated according to Eq. (1) from results given in column 5 and 6 and referenced to 298 K.

<sup>h</sup> Calculated according to Eq. (1) from results given in column 5 and 6 and adjusted to 400 K or 500 K according to the Kirchhoff's Law

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