Article

Thermodynamics of Reversible Hydrogen Storage: Are Methoxy-Substituted Biphenyls Better through Oxygen Functionality?

Sergey P. Verevkin [1,2,*], Artemiy A. Samarov [3] and Sergey V. Vostrikov [4]

1 Competence Centre CALOR, Faculty of Interdisciplinary Research, University of Rostock, 18059 Rostock, Germany
2 Department of Physical Chemistry, Kazan Federal University, 420008 Kazan, Russia
3 Department of Chemical Thermodynamics and Kinetics, Saint Petersburg State University, 198504 Saint Petersburg, Russia; samarov@yandex.ru
4 Chemical-Technological Department, Samara State Technical University, 443100 Samara, Russia; vosser@mail.ru
* Correspondence: sergey.verevkin@uni-rostock.de

Abstract: The reversible hydrogenation/dehydrogenation of aromatic molecules, known as liquid organic hydrogen carriers, is considered as an attractive option for the safe storage and release of elemental hydrogen. The recently reported efficient synthetic routes to obtain methoxy-biphenyls in high yield make them promising candidates for hydrogen storage. In this work, a series of methoxy-substituted biphenyls and their structural parent compounds were studied. The absolute vapour pressures were measured using the transpiration method and the enthalpies of vaporisation/sublimation were determined. We applied a step-by-step procedure including structure–property correlations and quantum chemical calculations to evaluate the quality of thermochemical data on the enthalpies of phase transitions and enthalpies of formation of the studied methoxy compounds. The data sets on thermodynamic properties were evaluated and recommended for calculations in chemical engineering. A thermodynamic analysis of chemical reactions based on methoxy-biphenyls in the context of hydrogen storage was carried out and the energetics of these reactions were compared with the energetics of reactions of common LOHCs. The influence of the position of the methoxy groups in the rings on the enthalpies of the reactions relevant for hydrogen storage was discussed.

Keywords: hydrogen storage; LOHC; enthalpies of phase transitions; enthalpy of formation; vapour pressure; structure–property correlation; quantum chemical calculations

1. Introduction

The sustainable development of technologies using renewable energy sources such as wind, solar, biomass, or geothermal instead of traditional fossil energy sources is the obvious trend of the last decades. Currently, one of the most promising concepts for the alternative energy sources is based on the conversion of the redundant electrical energy obtained from the sun, wind, etc., into elemental hydrogen to be used as an energy carrier. Conventional compression or liquefaction of hydrogen is challenging and not safe enough. In contrast, the LOHCs (or chemical hydrides) have the advantage of storing a sufficient amount of hydrogen at ambient temperatures and releasing it through reversible catalytic dehydrogenation processes over several cycles.

Generally, all compounds containing the double bonds in the molecule can be considered as a potential LOHC. However, if hydrogenation of the double bonds is the thermodynamically favourable reaction, reverse dehydrogenation is thermodynamically very unfavourable and requires high temperatures to shift the equilibrium toward sufficient hydrogen release. The dehydrogenation temperature is directly related to the chemical

structures of the hydrogen-lean and hydrogen-rich counterparts of the LOHC system. Understanding the general regularities between the structures of the LOHC counterparts and their thermodynamic properties is the only way to find the optimal compounds for practical applications. The present work extends our previous efforts [1] to establish these general regularities via thermochemical studies of LOHC systems based on methoxy-substituted biphenyls, as shown in Figure 1.
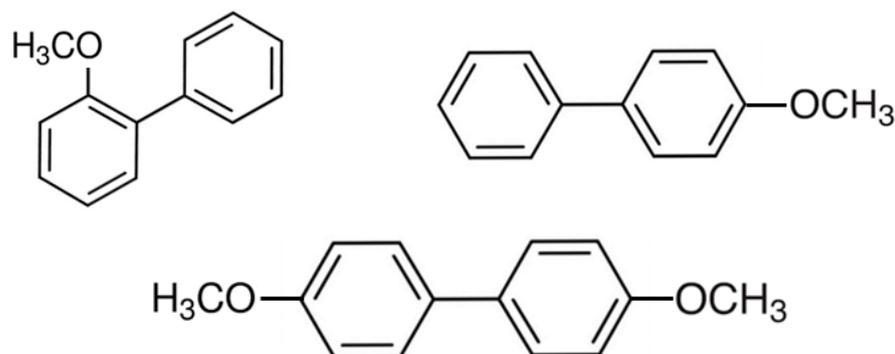

Figure 1. Structures of methoxy-biphenyls studied in this work: 2-methoxy-biphenyl, 4-methoxy-biphenyl, and 4,4′-dimethoxy-biphenyl.

The recently reported efficient synthetic routes to obtain these materials in high yield [2–4] make them promising candidates for hydrogen storage. The practically relevant LOHC systems and chemical reactions of the reversible hydrogen storage are given in Figure 2.
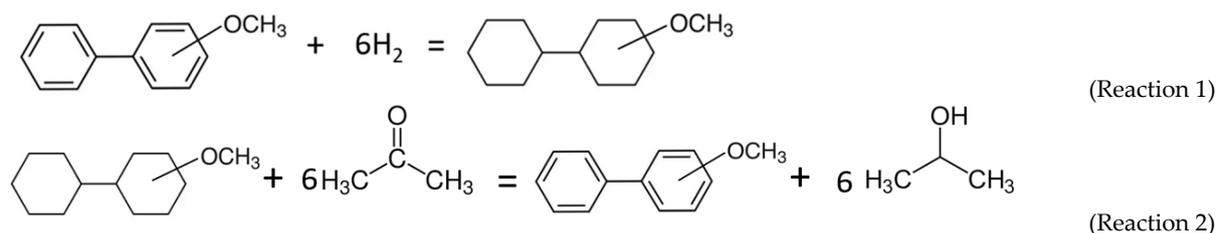

(Reaction 1)

(Reaction 2)

Figure 2. Chemical reactions of the reversible hydrogen storage using methoxy-biphenyls as the liquid organic hydrogen carriers (LOHCs).

The perhydrogenated methoxy-bicyclohexanes formed in the Reaction 1 may be involved in the transfer hydrogenation (TH) reactions (see Reaction 2). The transfer hydrogenation reactions can be considered as an attractive alternative to the reversible catalytic hydrogenation/dehydrogenation systems, since these reactions occur under mild conditions without expensive high-pressure reactors [5]. The TH reactions are very suitable for feeding fuel cells, e.g., for the reduction of acetone to the corresponding iso-propanol [6], using perhydro-dibenzyltoluene and platinum-on-silica (Pt/SiO$_2$) catalyst [7]. Oxygenated LOHC systems have been shown to release hydrogen efficiently, especially at low temperatures, and have a high storage capacity, which makes them attractive for technical applications [8]. Consequently, alkoxy-naphthalenes/alkoxy-bicyclohexanes are also expected to be efficient as LOHC systems.

2. Methodology

The hydrogenation/dehydrogenation reactions proceed under pressure, and the reactants are generally liquid under the reaction conditions (with the exception of hydrogen). The hydrogenation/dehydrogenation reaction enthalpies, $\Delta_r H_m^o$, for any liquid-phase hydrogen storage LOHC system are usually calculated from the standard molar liquid phase enthalpies of the formation of reactants, $\Delta_f H_m^o$(liq), using Hess's Law. With increasing interest in reversible hydrogen storage, it is impractical to measure $\Delta_f H_m^o$(liq) values for

the numerous LOHC systems that hold promise for the future. Therefore, a judicious combination of experimental, empirical, and quantum chemical (QC) methods seems to be the only way forward in the thermodynamic analysis and selection of LOHC systems of industrial interest. In particular, the use of modern QC methods enables a significant acceleration in the screening of promising LOHC systems, since standard molar gas phase formation enthalpies, $\Delta_f H_m^o$(liq), calculated using high-level methods nowadays reach a "chemical accuracy" of ± 4–5 kJ·mol^{-1} [9].

The quantum chemical gas-phase enthalpies of formation and the practically important liquid phase enthalpies of formation are related via the textbook equation

$$\Delta_f H_m^o(\text{liq, } 298.15 \text{ K}) = \Delta_f H_m^o(\text{g, } 298.15 \text{ K}) - \Delta_l^g H_m^o(298.15 \text{ K}) \tag{1}$$

where $\Delta_l^g H_m^o(298.15 \text{ K})$ is the standard molar enthalpy of vaporisation. In our experience, $\Delta_l^g H_m^o(298.15 \text{ K})$ values can be relatively easily measured using various methods or estimated using various group additivity rules and structure–property correlations. Under the latter prerequisite, a reasonable roadmap can be proposed to comprehensively obtain the thermodynamic quantities essential for reversible hydrogen storage.

- *Step I*: the possible experimental and empirical methods are involved to obtain and validate the $\Delta_l^g H_m^o(298.15 \text{ K})$ values;
- *Step II*: the high-level quantum chemical calculations are performed to compute $\Delta_f H_m^o(\text{g, } 298.15 \text{ K})$ values and the possible experimental and empirical methods are involved to validate these results;
- *Step III*: the liquid-phase $\Delta_f H_m^o(\text{liq, } 298.15 \text{ K})$ values are derived according to Equation (1) and a thermodynamic analysis of the LOHC system is performed.

This roadmap helps to follow the logic of the combination of experimental and theoretical methods used in this work to evaluate the practical potential of the methoxy-biphenyl/methoxy-bicyclohexyl LOHC systems.

3. Experimental

3.1. Materials

The samples of methoxy-biphenyls used in this work were commercially available (see Table S1). They were additionally purified before the thermochemical measurements. Purities better than a 0.9998 mass fraction were determined using gas–liquid chromatography on the capillary column. Details on purification and purity determination are given in ESI.

3.2. Experimental and Theoretical Methods

The absolute vapour pressures over methoxy-biphenyls were measured using the transpiration method. A nitrogen stream was passed through the saturator filled with the sample at various constant temperatures (± 0.1 K). To eliminate hydraulic resistance and create sufficient contact area between the sample and the nitrogen stream, the sample was spread over the small glass beads. After saturation equilibrium was reached, the material transported by the gas stream was collected in a cold trap and its amount determined using GC. The temperature dependences of the absolute vapour pressures for each compound were used to calculate thermodynamic functions of vaporisation/sublimation of methoxy-biphenyls. A concise description and the necessary details are given in ESI.

The melting temperatures and enthalpies of fusion for 4-methoxy-biphenyl and 4,4′-dimethoxy-biphenyl were measured via DSC. The necessary experimental details are given in ESI.

The Gaussian 16 series [10] software was used for quantum chemical (QC) calculations. The H_{298} enthalpies of the most stable conformers were calculated using the G4 method [11] and they were finally converted to the theoretical $\Delta_f H_m^o(\text{g, } 298.15 \text{ K})$ values and discussed.

4. Results and Discussion

4.1. Step I: Experimental Absolute Vapour Pressures

The vapour pressure–temperature dependencies for methoxy-biphenyls were measured using the transpiration method and fitted using the following equation:

$$R \cdot \ln(p_i / p_{ref}) = a + \frac{b}{T} + \Delta_{cr,l}^g C_{p,m}^o \cdot \ln\left(\frac{T}{T_0}\right) \tag{2}$$

where R = 8.314462 J·K^{-1}·mol^{-1} is the molar gas constant, the reference pressure $p_{ref} = 1$ Pa, a and b are adjustable parameters, the arbitrary temperature T_0 applied in Equation (2) was chosen to be T_0 = 298.15 K, and $\Delta_{cr,l}^g C_{p,m}^o = C_{p,m}^o(\text{g}) - C_{p,m}^o(\text{cr or liq})$ is the difference between the molar heat capacities of the gaseous $C_{p,m}^o(\text{g})$ and the crystal or liquid phase $C_{p,m}^o(\text{cr or liq})$, respectively. The differences $\Delta_{cr,l}^g C_{p,m}^o$ used in Equation (2) are compiled in Table S2. The vapour pressures measured in this work and fitting parameters of Equation (2) are collected in Table 1.

The systematic vapour pressure measurements for 2- and 4-methoxy-biphenyls were performed for the first time. It turned out that the single experimental boiling temperatures at various reduced pressures found in the literature (see Table S3) can be used to support these new results. These boiling points are usually measured during purification of the synthesised product and are used to characterise the compound. As a rule, the pressures are determined using non-calibrated manometers and the boiling temperatures are usually monitored in the range of a few degrees. Recently [12], however, we have shown that even from such rough data, reasonable trends can generally be derived and used for comparison if no systematic vapour pressures are available. The boiling temperatures compiled for methoxy-biphenyls in Table S3 were measured at the elevated temperature and cannot be directly compared to the "low temperature" transpiration results. However, the $\Delta_l^g H_m^o(298.15 \text{ K})$ values derived from these literature results can be fairly compared to the results of this work, as shown in Section 4.2.

4.2. Step I: Experimental Standard Molar Enthalpies of Sublimation/Vaporisation from Vapour Pressure Measurements

The molar vaporisation/sublimation enthalpies of methoxy-biphenyls were derived from the temperature dependences of the vapour pressures, approximated by Equation (3) using the following equation:

$$\Delta_{cr,l}^g H_m^o(T) = -b + \Delta_{cr,l}^g C_{p,m}^o \times T \tag{3}$$

where b is one of the adjustable parameters of Equation (3). The vaporisation/sublimation enthalpies $\Delta_{cr,l}^g H_m^o(298.15 \text{ K})$ of the methoxy-biphenyls were calculated with help of Equations (2) and (3) with the $\Delta_{cr,l}^g C_{p,m}^o$ values from Table S2. Details of the calculation procedures can be found in ESI. As mentioned in the introduction, in this work the auxiliary sets of the perhydrogenated methoxy-biphenyls (methoxy-bicyclohexanes) and structurally similar molecules of methoxy-iso-propylbenzenes and their perhydrogenated products (methoxy-iso-propyl-cyclohexanes) were studied using empirical methods. The boiling points available in the literature were collected for each compound and also treated using Equations (2) and (3) to calculate the vaporisation enthalpies at 298.15 K. The uniformly treated results are summarized for comparison in Table 2.

The standard molar vaporisation enthalpy for 2-methoxy-biphenyl as well as the standard molar vaporisation/sublimation enthalpies for 4-methoxy-biphenyl were derived for the first time. As can be seen from Table 2, the enthalpy of vaporisation calculated from the boiling points (BP) for 4-methoxybiphenyl, $\Delta_l^g H_m^o(298.15 \text{ K})$ = (76.5 ± 5.0) kJ·mol^{-1}, agrees within the experimental uncertainties with the more accurate experimental result, $\Delta_l^g H_m^o(298.15 \text{ K})$ = (79.9 ± 0.9) kJ·mol^{-1}, measured using the transpiration method. Also,

the sufficient consistency of solid–liquid, liquid–gas, and solid–gas phase transitions for 4-methoxybiphenyl is shown in Table 3.

Table 1. Vapour pressures p and standard molar functions of sublimation/vaporisation measured in this work using the transpiration method.

$T/$ 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	$\Delta_{cr,l}^{g} H_m^{o}/$ kJ$\cdot$mol^{-1}	$\Delta_{cr,l}^{g} S_m^{o}/$ J$\cdot$K$^{-1}\cdot$mol^{-1}
2-methoxybiphenyl (liq) $\Delta_l^g H_m^o(298.15 \text{ K}) = (57.8 \pm 0.5)$ kJ$\cdot$mol^{-1}								
$\Delta_l^g S_m^o(298.15 \text{ K}) = (122.4 \pm 1.2)$ J$\cdot$K$^{-1}\cdot$mol^{-1}								
$\Delta_l^g G_m^o(298.15 \text{ K}) = (21.3 \pm 0.1)$ kJ$\cdot$mol^{-1}								
$\ln(p/p_{\text{ref}}) = \frac{283.9}{R} - \frac{77384.1}{RT} - \frac{65.8}{R} \times (\ln\frac{T}{298.15}); p_{\text{ref}} = 1$ Pa								
283.3	1.78	4.549	297.2	4.71	5.34	0.16	58.7	125.6
286.3	1.99	3.876	297.6	4.85	7.01	0.20	58.5	125.0
288.7	1.92	3.006	297.6	4.75	8.67	0.24	58.4	124.5
290.4	2.02	2.749	298.1	4.71	9.99	0.27	58.3	124.1
292.6	2.27	2.556	298.1	4.79	12.02	0.33	58.1	123.7
293.2	2.15	2.304	297.2	4.77	12.63	0.34	58.1	123.5
296.4	2.81	2.317	298.1	4.79	16.40	0.44	57.9	122.9
297.9	2.31	1.739	295.9	4.85	17.84	0.47	57.8	122.2
300.4	1.88	1.124	298.1	2.25	22.56	0.59	57.6	122.0
301.9	2.58	1.386	298.1	2.25	25.17	0.65	57.5	121.7
302.9	5.49	2.705	295.9	4.85	27.17	0.70	57.5	121.5
305.1	2.03	0.861	298.1	2.25	31.74	0.82	57.3	120.9
307.9	6.97	2.423	297.7	4.85	38.71	0.99	57.1	120.2
309.2	3.15	0.995	298.1	2.30	42.61	1.09	57.0	120.0
312.9	6.66	1.615	297.7	4.85	55.44	1.41	56.8	119.2
315.1	3.59	0.765	297.2	2.30	62.89	1.60	56.7	118.5
317.9	13.26	2.261	297.7	4.85	78.81	2.00	56.5	118.2
319.3	5.30	0.842	297.2	2.30	84.44	2.14	56.4	117.8
323.3	4.77	0.574	298.2	2.30	111.9	2.82	56.1	117.1
4-methoxybiphenyl (liq) $\Delta_l^g H_m^o(298.15 \text{ K}) = (79.9 \pm 0.9)$ kJ$\cdot$mol^{-1}								
$\Delta_l^g S_m^o(298.15 \text{ K}) = (153.4 \pm 2.6)$ J$\cdot$K$^{-1}\cdot$mol^{-1}								
$\Delta_l^g G_m^o(298.15 \text{ K}) = (34.1 \pm 0.1)$ kJ$\cdot$mol^{-1}								
$\ln(p/p_{\text{ref}}) = \frac{337.4}{R} - \frac{105868.7}{RT} - \frac{89.9}{R} \times (\ln\frac{T}{298.15}); p_{\text{ref}} = 1$ Pa								
363.8	1.82	0.799	295.0	3.69	30.36	0.78	75.5	140.3
366.5	1.85	0.671	295.0	1.49	36.65	0.94	75.4	139.9
371.8	2.21	0.573	295.0	1.72	51.34	1.31	75.0	138.8
376.3	2.51	0.487	295.0	1.72	68.51	1.74	74.7	138.0
381.7	2.97	0.401	295.0	1.72	98.32	2.48	74.4	137.3
385.5	4.00	0.430	295.0	1.72	123.6	3.11	74.1	136.6
390.7	5.71	0.459	295.0	1.72	165.5	4.16	73.8	135.6
395.5	7.20	0.444	295.0	1.72	215.2	5.40	73.4	134.7
400.6	9.48	0.430	295.0	1.72	292.8	7.34	73.1	134.0
4-methoxybiphenyl (cr) $\Delta_{cr}^g H_m^o(298.15 \text{ K}) = (99.8 \pm 0.7)$ kJ$\cdot$mol^{-1}								
$\Delta_{cr}^g S_m^o(298.15 \text{ K}) = (208.5 \pm 1.6)$ J$\cdot$K$^{-1}\cdot$mol^{-1}								
$\Delta_{cr}^g G_m^o(298.15 \text{ K}) = (37.7 \pm 0.1)$ kJ$\cdot$mol^{-1}								
$\ln(p/p_{\text{ref}}) = \frac{340.8}{R} - \frac{110732.8}{RT} - \frac{36.5}{R} \times \ln(\frac{T}{298.15}); p_{\text{ref}} = 1$ Pa								
313.1	1.31	103.9	295.0	9.98	0.17	0.01	99.3	206.7
323.3	1.00	23.28	295.0	9.98	0.57	0.02	98.9	205.7
328.3	1.03	13.80	295.0	9.98	0.99	0.03	98.8	205.0
333.5	0.91	6.970	295.0	6.15	1.73	0.05	98.6	204.4
338.3	0.87	3.998	295.0	6.15	2.89	0.08	98.4	204.0
343.3	2.07	5.820	295.0	9.98	4.72	0.12	98.2	203.3
348.1	2.24	3.822	295.0	9.97	7.81	0.22	98.0	203.0
353.8	0.91	0.922	295.0	3.69	13.10	0.35	97.8	202.2
356.1	11.27	8.951	295.0	9.95	16.76	0.44	97.7	202.2
358.9	1.56	0.984	295.0	3.69	21.11	0.55	97.6	201.7
362.4	2.83	1.291	295.0	3.69	29.14	0.75	97.5	201.4

[a] Saturation temperature measured using standard uncertainty ($u(T) = 0.1$ K). [b] Mass of transferred sample condensed at $T = 273$ 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 the measurement of the gas flow. [e] Vapour pressure is given at temperature T, calculated from the m and the residual vapour pressure at the condensation temperature calculated using an iteration procedure.

Table 2. Compilation of the enthalpies of vaporisation/sublimation, $\Delta^{\text{g}}_{\text{l,cr}}H^{\text{o}}_{\text{m}}$, of methoxy-biphenyls (in kJ·mol^{-1}).

Compounds/CAS	Method [a]	*T*-Range/K	$\Delta^{\text{g}}_{\text{l,cr}}H^{\text{o}}_{\text{m}}$ T_{av}	$\Delta^{\text{g}}_{\text{l,cr}}H^{\text{o}}_{\text{m}}$ 298.15 K	Ref
3-methoxy-biphenyl (liq) 2113-56-6	BP J_x	358–566	67.2 ± 1.9	77.1 ± 2.7 79.3 ± 1.5 **78.8 ± 1.3** [b]	Table S3 Table S4 average
2-methoxy-biphenyl (liq) 86-26-0	T J_x	283.3–323.3	57.5 ± 0.4	57.8 ± 0.5 57.6 ± 1.0 **57.8 ± 0.4** [b]	Table 1 Table S5 average
4-methoxy-biphenyl (liq) 613-37-6	T BP J_x	363.8–400.6 430–573	74.4 ± 0.8 63.3 ± 4.2	79.9 ± 0.9 76.5 ± 5.0 **79.9 ± 0.6** [b] 79.3 ± 1.5	Table 1 Table S3 average Table S4
4-methoxy-biphenyl (cr) 613-37-6	T PhT	313.1–362.4	98.4 ± 0.5	99.8 ± 0.7 99.3 ± 1.4 **99.7 ± 0.6** [b]	Table 1 Table 3 average
4,4′-dimethoxy-biphenyl (liq) 2132-80-1	BP J_x	388–611	78.1 ± 1.8	92.4 ± 3.2 91.8 ± 1.5 **91.9 ± 1.4** [b]	Table S3 Table S4 average
2-methoxy-iso-propylbenzene (liq) 2944-47-0	BP J_x	307–474	45.4 ± 3.6	50.9 ± 3.8 51.6 ± 1.0 **51.6 ± 0.9** [b]	Table S3 Table S5 average
3-methoxy-iso-propylbenzene (liq) 6380-20-7	BP J_x	332–484	49.9 ± 2.2	56.6 ± 2.6 58.3 ± 1.5 **57.9 ± 1.3** [b]	Table S3 Table S4 average
4-methoxy-iso-propylbenzene (liq) 4132-48-3	BP J_x	331–488	51.0 ± 1.6	57.6 ± 2.1 58.8 ± 1.5 **58.4 ± 1.2** [b]	Table S3 Table S4 average
1-methoxy-2-iso-propyl-cyclohexane 103754-94-5	T_b			50.7 ± 0.6	Table S11
methoxy-cyclohexane (liq) 931-56-6	BP T_b J_x CP	308–409	39.6 ± 1.8	42.7 ± 1.9 42.9 ± 0.6 42.8 ± 1.0 43.2 ± 1.0 **43.0 ± 0.5** [b]	Table S3 Table S11 Table S6 This work average
2-methoxy-bicyclohexane (liq) 764717-18-2	CP			66.1 ± 1.5	This work
3-methoxy-bicyclohexane (liq) 2447033-60-3	CP			69.3 ± 1.5	This work
4-methoxy-bicyclohexane (liq) 160153-88-8	CP			69.3 ± 1.5	This work
4,4′-dimethoxy-bicyclohexane (liq) 316363-49-2	CP			79.2 ± 1.5	This work

[a] Methods: T = transpiration method; J_x = from correlation with Kovats indices; PhT = from consistency of phase transitions (see Table 3); CP = calculated according to the "centerpiece" approach (see text); T_b = from correlation with the normal boiling temperatures; BP = from boiling points at various pressures (see Table S3). [b] Weighted mean value (uncertainties were taken as the weighting factor). Values given in bold are recommended for further thermochemical calculations.

Table 3. Enthalpies of fusion ($\Delta_{cr}^l H_m^o$), vaporisation ($\Delta_l^g H_m^o$), and sublimation ($\Delta_{cr}^g H_m^o$) of methoxy-biphenyls at melting points (T_{fus}) and 298 K (in kJ·mol^{-1}) [a].

Compound	T_{fus} K	$\Delta_{cr}^l H_m^o(T_{fus})$ kJ·mol^{-1}	$\Delta_{cr}^l H_m^o$ (298 K) [b] kJ·mol^{-1}	$\Delta_l^g H_m^o$ (298 K) kJ·mol^{-1}	$\Delta_{cr}^g H_m^o$ (298 K) kJ·mol^{-1}
4-methoxy-biphenyl	363.1	22.9 ± 0.2	19.4 ± 1.1	79.9 ± 0.9 [c]	99.3 ± 1.4 [d]
4,4′-dimethoxy-biphenyl	450.9	35.2 ± 0.3	25.9 ± 2.8	91.9 ± 1.4 [c]	117.8 ± 3.1 [d]

[a] Uncertainties are presented as expanded uncertainties (0.95 level of confidence with k = 2). [b] The $\Delta_{cr}^l H_m^o$ at T_{fus} values were adjusted to 298.15 K as shown in ESI. Uncertainties of $\Delta_{cr}^l H_m^o$(298 K) were estimated with 30% of the total adjustment. [c] Enthalpies of vaporisation evaluated in Table 2. [d] Sum of columns 4 and 5 in this table.

Indeed, the sublimation, vaporisation, and fusion enthalpies are related by Equation (4):

$$\Delta_{cr}^g H_m^o(298.15\ \text{K}) = \Delta_l^g H_m^o(298.15\ \text{K}) + \Delta_{cr}^l H_m^o(298.15\ \text{K}) \tag{4}$$

when all enthalpies are adjusted to the common temperature T = 298.15 K as explained in ESI. The 4-methoxybiphenyl is solid at room temperatures. The solid–liquid, liquid–gas, and solid–gas phase transitions for this compound are summarised in Table 3. The vaporisation enthalpy, $\Delta_l^g H_m^o$(298.15 K) = (79.9 ± 0.6) kJ·mol^{-1}, was evaluated in Table 2 using the BP and transpiration results. The latter value, together with the fusion enthalpy, $\Delta_{cr}^l H_m^o$(298.15 K) = (19.4 ± 1.1) kJ·mol^{-1}, estimated in Table 3 gives an "empirical" sublimation enthalpy of 4-methoxybiphenyl of $\Delta_{cr}^g H_m^o$(298.15 K) = 79.9 + 19.4 = (99.3 ± 1.4) kJ· mol^{-1}. This result is in excellent agreement with the experimental sublimation enthalpy, $\Delta_{cr}^g H_m^o$(298.15 K) = (99.8 ± 0.7) kJ·mol^{-1} (see Table 2), demonstrating the consistency of the phase transition data for this compound. Similarly, the sublimation data for methyl 4,4′-dimethoxybiphenyl were calculated (see calculations in Table 3 and the evaluated value in Table 2). Unfortunately, for all other entries in Table 2, there are no experimental data for comparison. Therefore, any type of validation of $\Delta_l^g H_m^o$(298.15 K) values is required for the compounds of interest listed in Table 2.

4.3. Step I: Validation of Vaporisation Enthalpies Using Structure–Property Correlations

Structure–property correlations are one of the basic principles of physical chemistry. This type of correlation helps to establish consistency in the new experimental results with the network of physicochemical data already available for similarly shaped molecules.

4.3.1. Correlation with the Kovats Indices J_x

The Kovats retention indices, J_x, are values that are readily measurable using gas chromatography (GC) [13]. The $\Delta_l^g H_m^o$(298.15 K) values in structural parent series of molecules usually correlate linearly with the Kovats indices. The Kovats indices of 3- and 4-substituted methoxy-biphenyls, methoxy-benzenes, and alkyl phenyl ethers on non-polar column Ultra 1 (see Table S4) were taken from the literature [14].

The collected $\Delta_l^g H_m^o$(298.15 K) values in Table S4 show a very good linear correlation with the corresponding J_x values:

$$\Delta_l^g H_m^o(298.15\ \text{K}) = 5.6 + 0.0459 \times J_x \ \text{ with } R^2 = 0.9914. \tag{5}$$

Table S4 (column 6) shows that the differences between experimental values and those calculated according to Equation (5) values are mostly below 1.5 kJ·mol^{-1}. The "empirical" enthalpies of vaporisation derived from Equation (5) (see Table S4, column 5) are referred to as J_x values in Table 2 and agree well with results obtained using other methods.

It has been found that the "ortho"-methoxy-substituted molecules (see Table S5) are in a separate line in this type of correlation:

$$\Delta_l^g H_m^o(298.15\ \text{K}) = 34.6 + 0.0152 \times J_x \ \text{ with } R^2 = 0.9775. \tag{6}$$

However, such behaviour is typical for the methoxy-substituted benzenes [15].

Table S5 (column 6) shows that the disagreement between values calculated according to Equation (6) and the experimental values is well below 1.0 kJ·mol^{-1}. The "empirical" enthalpies of vaporisation derived from Equation (6) (see Table S5, column 5) also agree well with results obtained using other methods, as shown in Table 2.

Similarly, we correlated the $\Delta_l^g H_m^o$(298.15 K) values of di-alkyl ethers with the corresponding J_x values (see Tables S6 and S7) to obtain the auxiliary value of the enthalpy of vaporisation of methoxy-cyclohexane, which is needed for the thermochemical calculations in this work. The value $\Delta_l^g H_m^o$(298.15 K) = 42.8 ± 1.0 kJ·mol^{-1} obtained in this way is in excellent agreement with the results obtained using other methods, as shown in Table 2.

4.3.2. Correlation Vaporisation Enthalpies of the Parent Structures

It is obvious that methoxy-biphenyls and the hydroxy-biphenyls (or phenyl-phenols) are structurally related. Therefore, a correlation of the experimental $\Delta_l^g H_m^o$(298.15 K) values for the series of methoxy-biphenyls with the experimental vaporisation enthalpies for the series of hydroxy-biphenyls was obtained. The vaporisation enthalpies for the latter series were well established in our earlier work (see Tables S8–S10). The summary of experimental data for this correlation is given in Table 4.

Table 4. Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$(298.15 K), of hydroxy-biphenyls and methoxy-biphenyls (in kJ·mol^{-1}).
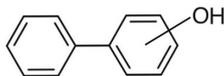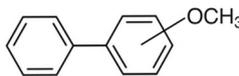
hydroxy-biphenyls	$\Delta_l^g H_m^o$ (exp) [a]	*methoxy-biphenyls*	$\Delta_l^g H_m^o$ (exp) [b]
2-hydroxy-biphenyl	72.6 ± 1.4	2-methoxy-biphenyl	57.8 ± 0.4
3-hydroxy-biphenyl	85.0 ± 1.0	3-methoxy-biphenyl	78.8 ± 1.3
4-hydroxy-biphenyl	85.5 ± 3.0	4-methoxy-biphenyl	79.9 ± 0.9

[a] Experimental data evaluated in Tables S8 and S9. [b] Experimental data evaluated in Table 2.

As is apparent from Table 4, the vaporisation enthalpies of 2-substituted biphenyls are drastically lower compared to those of 3- and 4-substituted biphenyls. The vaporisation enthalpies of 3- and 4- isomers are indistinguishable within their experimental uncertainties. Such behaviour is typical for ortho-, meta-, and para-substituted benzenes [15]. The correlation of the vaporisation enthalpies, $\Delta_l^g H_m^o$(298.15 K), of hydroxy-biphenyls and methoxy-biphenyls exhibits a practically straight line (see Figure 3, left), which can be taken as an indicator of the internal consistency of the $\Delta_l^g H_m^o$(298.15 K) values in both series.
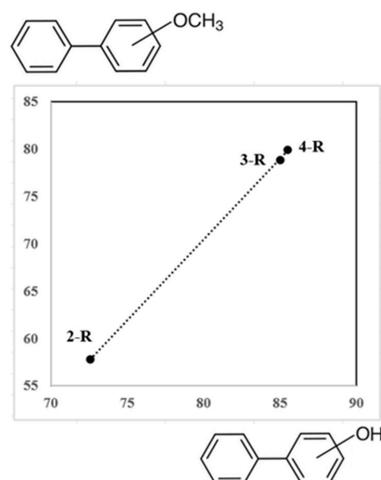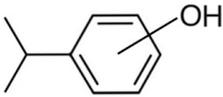

Figure 3. Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$(298.15 K), of hydroxy-biphenyls and methoxy-biphenyls. All values are in kJ·mol^{-1} with R = position of the substituent on the benzene ring.

Structurally, the series of hydroxy-iso-propylbenzenes and methoxy-iso-propylbenzenes is quite comparable with the series of hydroxy-biphenyls and methoxy-biphenyls shown in Figure S1. The correlation of the $\Delta_l^g H_m^o$(298.15 K) values of hydroxy-iso-propylbenzenes and methoxy-iso-propylbenzenes (see Table 5) also exhibits a practically straight line (see Figure S1), and it is considered as proof for the consistency of evaluated vaporisation enthalpies of methoxy-iso-propylbenzenes with the reliable set of data for hydroxy-iso-propylbenzenes (see Tables S8–S10).

Table 5. Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$(298.15 K), of hydroxy-iso-propylbenzenes and methoxy-iso-propylbenzenes (in kJ·mol^{-1}).

hydroxy-iso-propylbenzenes	$\Delta_l^g H_m^o$(exp) [a]	*methoxy-iso-propylbenzenes*	$\Delta_l^g H_m^o$(exp) [b]
2-hydroxy-iso-propylbenzene	64.4 ± 1.4	2-methoxy-iso-propylbenzene	51.6 ± 0.9
3-hydroxy-iso-propylbenzene	70.4 ± 1.0	3-methoxy-iso-propylbenzene	58.3 ± 1.5
4-hydroxy-iso-propylbenzene	70.3 ± 1.2	4-methoxy-iso-propylbenzene	58.4 ± 1.2

[a] Experimental data evaluated in Tables S8–S10. [b] Experimental data evaluated in Table 2.

An interesting energetic aspect in structurally related behaviour is revealed by comparing the quantitative differences in in $\Delta_l^g H_m^o$(298.15 K) values: between para- and ortho-methoxy biphenyls and between para- and ortho-methoxy iso-propylbenzenes and the corresponding differences between para- and ortho-hydroxy biphenyls and for the para- and ortho-hydroxy iso-propylbenzenes, as shown in Figure 4.
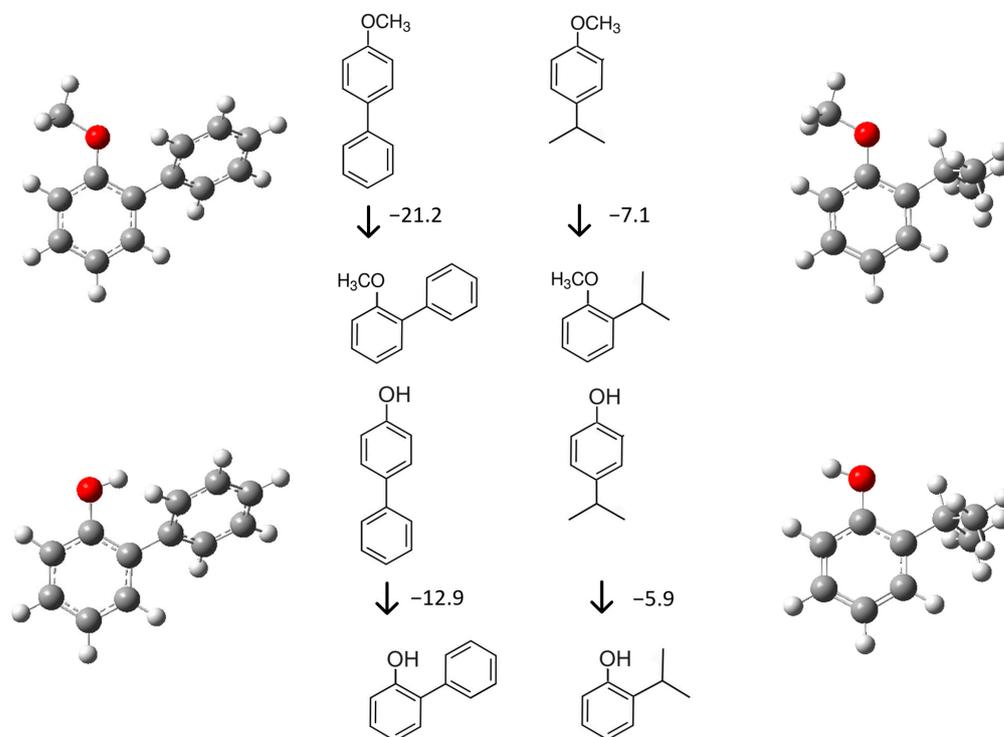

Figure 4. Comparison of the quantitative differences in $\Delta_l^g H_m^o$(298.15 K)-values: between para- and ortho-methoxy-biphenyls and between para- and ortho-methoxy-iso-propylbenzenes (**left**) and the corresponding differences between para- and ortho-hydroxy-biphenyls and between para- and ortho-hydroxy-iso-propylbenzenes (**right**). Numerical data are given in Tables S8 and S10. All values are in kJ·mol^{-1}.

It can be seen from Figure 4 that the differences in $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) values between para- and ortho-methoxy-iso-propylbenzenes, $\Delta = -7.1$ kJ·mol^{-1}, and the corresponding differences between para- and ortho-hydroxy-iso-propylbenzenes, $\Delta = -5.9$ kJ·mol^{-1}, are quite comparable in magnitude. It can be concluded that ortho-methoxy and ortho-hydroxy substituents have a similar effect on reducing the enthalpies of vaporisation compared to the corresponding para-methoxy and para-hydroxy substituents on iso-propylbenzene. Similar behaviour was expected for the interplay of the methoxy- and hydroxy- substituents on the biphenyl, considering that iso-propyl and phenyl are not spatially significantly different. To our surprise, the differences in $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) values between para- and ortho-methoxy-biphenyls, $\Delta = -21.1$ kJ·mol^{-1}, and the corresponding differences between para- and ortho-hydroxy-biphenyls, $\Delta = -12.9$ kJ·mol^{-1}, are significantly different. How can this discrepancy be explained? Most likely, the reason is the intra-molecular hydrogen bonding specific to 2-phenylphenol. Indeed, it is known that in the liquid phase of such molecules the intermolecular hydrogen bond is predominant. However, upon leaving the liquid phase, the hydroxyl of the 2-phenylphenol immediately forms an intra-molecular H bond to the phenyl ring, which is in close proximity. The energy of this bond reduces the total energy required to evaporate 1 mole of 2-phenylphenol. In contrast, no intra- or inter-hydrogen bonding is possible in 2-methoxybiphenyl, and the very low enthalpy of vaporisation of this compound is due to the very loose packing of the sterically curled molecules. This plausible explanation for the energetic differences observed between the similarly shaped molecules is an indirect validation of the experimental and empirical vaporisation enthalpies of the methoxy-biphenyls evaluated in Table 2.

4.3.3. Correlation with Normal Boiling Points T_b

One of the quantitative methods of structure–property correlations is the correlation of vaporisation enthalpies with normal boiling points. The enthalpies of vaporisation of methoxy-cyclohexane and 1-methoxy-2-iso-propyl-cyclohexane are of interest for this work and their boiling temperatures are known. This type of correlation, therefore, makes it possible to obtain the desired property in an independent manner. The vaporisation enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), and normal boiling points, T_b, of di-alkyl ethers, methoxy-cyclohexane, and 1-methoxy-2-iso-propyl-cyclohexane (see Table S11) correlated as follows:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15 \text{ K}) = -22.2 + 0.01592 \times T_b \text{ with } \left(R^2 = 0.9930\right). \tag{7}$$

The "empirical" vaporisation enthalpy $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = 42.9 ± 0.6 kJ·mol^{-1} of methoxy-cyclohexane derived from Equation (7) (see Table S11, column 5) agrees well with the values obtained for this compound using other methods, as shown in Table 2. This good agreement can again be considered as evidence of good consistency of the experimental data included in the correlation and provides confidence the value $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) = 50.7 ± 0.6 kJ·mol^{-1} calculated for 1-methoxy-2-iso-propyl-cyclohexane according to Equation (7). As is finally shown in Table 2, various structure–property correlations have definitely demonstrated the internal consistency of the datasets of methoxy-biphenyls, methoxy-iso-propylbenzenes, and methoxy-cyclohexane, evaluated in this table.

4.4. Step I: Calculation of Vaporisation Enthalpies Using the "Centerpiece" Group-Additivity Concept

The methoxy-di-cyclohexanes are involved in the hydrogenation/dehydrogenation reactions shown in Figure 2 as the hydrogen-rich counterpart of the LOHC system methoxy-biphenyl/methoxy-di-cyclohexane. Unfortunately, the experimental thermochemical data for these species are completely lacking. Numerous group additivity methods have been developed to predict both of the energetic properties, including enthalpies of formation and enthalpies vaporisation [16]. The idea behind conventional group additivity (GA) methods is to divide the structures of molecules into small groups and to attribute these groups to well-defined numerical contributions for the corresponding property of interest. For the

prediction, a frame of the desired molecule is collected from the corresponding number and type of these contributions. Recently, we modified the GA method and proposed a so-called "centerpiece" (CP) approach [17]. In this approach, a potentially large "centerpiece" molecule with a reliable enthalpy is selected. This "centerpiece" molecule should generally mimic the structure of other molecules of interest. Then, the required increments or groups (see Figure S2) are added to the "centerpiece" molecule, resulting in the frame of the desired molecule.

For example, bi-cyclohexane can serve as a perfect "centerpiece" for predicting the thermodynamic properties of methoxy-bi-cyclohexanes. The enthalpy of vaporisation (and also the enthalpy of formation) for this compound are well established (see Table S10). The idea is illustrated in Figure 5.
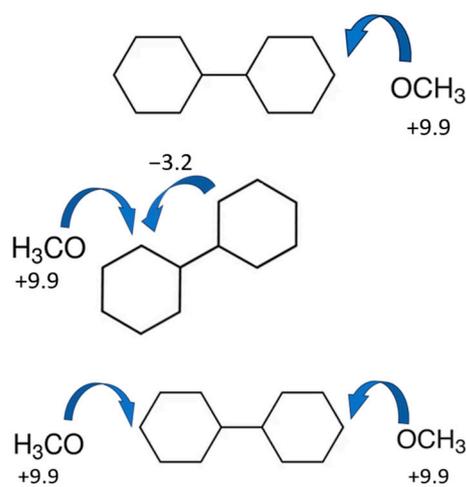

Figure 5. Calculating the enthalpy of vaporisation of methoxy-bi-cyclohexanes using the bi-cyclohexane as the "centerpiece".

To construct the 4-methoxy-bi-cyclohexane the contribution $H(C_6H) \rightarrow OCH_3$ = 9.9 kJ·mol^{-1} (see Figure S2) should be added to the vaporisation enthalpy of bi-cyclohexane $\Delta_l^g H_m^o$(298.15 K) = 59.4 ± 0.3 kJ·mol^{-1} (see Table S10). The resulting value $\Delta_l^g H_m^o$(298.15 K) = 69.3 ± 1.5 kJ·mol^{-1} (see Table 2) can be used for thermochemical calculations according to the reactions shown in Figure 2. To construct the 4,4′di-methoxy-bi-cyclohexane the two contributions $H(C_6H) \rightarrow OCH_3$ should be added to the vaporisation enthalpy of bi-cyclohexane as shown in Figure 5.

The construction of 2-methoxy-bi-cyclohexane is somewhat more demanding. For this molecule, an additional contribution for the steric interaction of methoxy-substituent and the adjacent cyclohexane ring is required (see Figure 6).
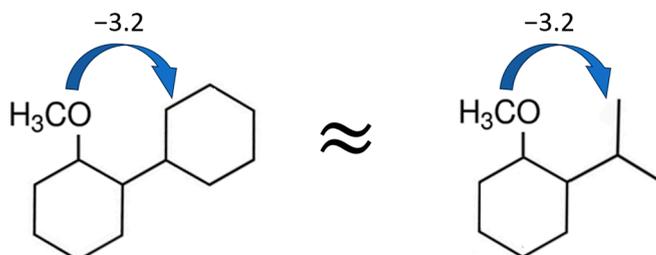

Figure 6. Calculating the ortho- interaction between methoxy-group and cyclohexane ring required for calculating the enthalpy of vaporisation of 2-methoxy-bi-cyclohexane using the bi-cyclohexane as the "centerpiece".

The latter contribution was derived as follows. Since thermodynamic data for 2-methoxy-bi-cyclohexane are completely lacking, we used the 2-methoxy-iso-propyl-cyclohexane to

model the required steric interaction, assuming that the spatial characteristics of the iso-propyl and cyclohexyl substituents are essentially similar. The calculation was based on the empirical value for 2-methoxy-iso-propyl-cyclohexane, $\Delta_l^g H_m^o$(298.15 K) = 50.7 $\pm$ 0.6 kJ·mol^{-1} (see Table 2). The "strain-free" reference value 53.9 $\pm$ 1.5 kJ·mol^{-1} for the vaporisation enthalpy of this compound was estimated using the summation enthalpy of vaporisation of methoxy-cyclohexane (Table 2) with the contribution H(C$_6$H)→iso-Pr given in Figure S2. The difference Δ = 50.7 − 53.9 = −3.2 kJ·mol^{-1} can be considered as a reasonable estimate for the decrease in vaporisation enthalpy due to steric repulsions of the substituents in both 2-methoxy-iso-propyl-cyclohexane and in the 2-methoxy-bi-cyclohexane. With this contribution, the vaporisation enthalpy of 2-methoxy-bi-cyclohexane $\Delta_l^g H_m^o$(298.15 K) = 66.1 $\pm$ 1.5 kJ·mol^{-1} (see Table 2) was assessed (see Table 2). The numerical values for the contributions that can be involved in the additive calculations of the hydrogen rich counterparts of the LOHC systems are given in ESI (see Figure S2 and Table S12).

Finally, with the comprehensive evaluation and validation of the $\Delta_l^g H_m^o$(298.15 K) values performed in Sections 4.3 and 4.4, the consistent set of vaporisation enthalpies was established. With the results evaluated in Table 2, the first step is completed. These results can now be combined with the $\Delta_f H_m^o$(g) values, which are calculated in the following second step.

4.5. Step II: Gas-Phase Enthalpies of Formation from Quantum Chemical Calculations

The most stable conformers for methoxy-biphenyls, methoxy-iso-propylbenzenes, and their perhydrogenated products (see Table S13) were found after conformational analysis performed using a computer code CREST [18]. The final optimisation was performed with the B3LYP/6-31g(d,p) method [19]. The G4 method was used to calculate the energies E_0 and the enthalpies H_{298} of the most stable conformers. The standard molar enthalpies of formation were derived from the resulting H_{298} enthalpies using the atomisation (AT) procedure [20] (e.g., for mono-methoxy-biphenyls)

$$C_{13}H_{12}O \rightarrow 13 \times C + 12 \times H + 1 \times O \tag{8}$$
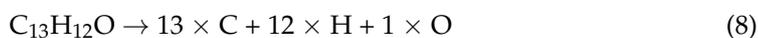
as well as using the well-balanced reactions (WBR) shown in Figure 7.
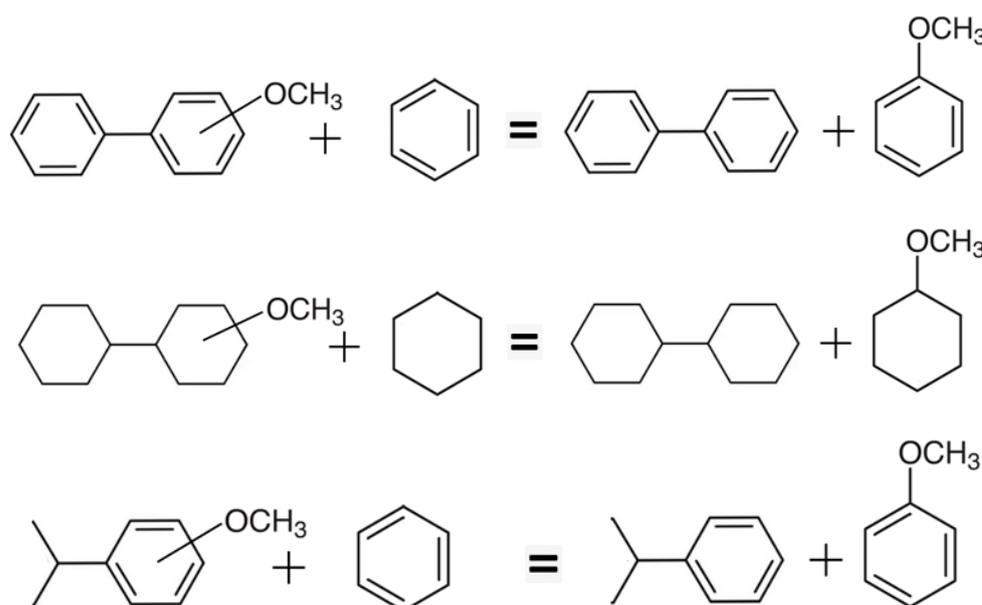

Figure 7. Well-balanced reactions used for calculating enthalpies of formation of methoxy-biphenyls, methoxy-bicyclohexanes, and methoxy-iso-propylbenzenes from the H_{298} enthalpies.

The *theoretical* gas-phase enthalpies of formation were calculated according to Hess's Law applied to reactions shown in Figure 7 using reliable experimental gas-phase enthalpies

of formation $\Delta_f H_m^o$(g, 298.15 K) of reactions participants (see Table S10). The results of the G4 quantum chemical calculations are summarised in Table 6.

Table 6. Comparison of gas-phase enthalpies of formation: calculated using G4, the centrepiece approach, and group additivity at T = 298.15 K (p° = 0.1 MPa) for methoxy-substituted biphenyls, iso-propyl-benzenes, and cyclohexanes (in kJ·mol^{-1}) [a].

Compound	$\Delta_f H_m^o$(g)$_{AT}$ [b]	$\Delta_f H_m^o$(g)$_{WBR}$ [c]	$\Delta_f H_m^o$(g)$_{CP}$ [d]	$\Delta_f H_m^o$(g)$_{GA}$ [e]
2-methoxy-biphenyl	25.3	32.0	-	-
3-methoxy-biphenyl	19.3	26.0	26.5	26.5
4-methoxy-biphenyl	20.2	26.9	26.5	26.5
4,4′-dimethoxy-biphenyl	−133.9	−125.6	−126.7	−126.7
2-methoxy-bicyclohexane	−367.5	−362.1	-	-
3-methoxy-bicyclohexane	−367.6	−362.2	−361.4	−367.3
4-methoxy-bicyclohexane	−366.9	−361.5	−361.4	−367.3
4,4′-dimethoxybicyclohexane	−516.8	−508.9	−508.7	−525.1
2-methoxy-iso-propylbenzene	−151.3	−146.1	-	-
3-methoxy-iso-propylbenzene	−155.1	−149.9	−149.2	−154.2
4-methoxy-iso-propylbenzene	−153.2	−148.0	−149.2	−154.2
1-methoxy-2-iso-propyl-cyclohexane	−346.1	−343.6	-	-
1-methoxy-3-iso-propyl-cyclohexane	−346.8	−344.3	−343.5	−349.5
1-methoxy-4-iso-propyl-cyclohexane	−346.0	−343.5	−343.5	−349.5

[a] The expanded uncertainties of the G4 method were assessed to be ±3.5 kJ·mol^{-1} [11]. [b] Calculated in this work according to the general atomisation reactions according to Equation (8). [c] Calculated in this work according to well-balanced reactions shown in Figure 7. [d] Calculated using the "centerpiece" approach as shown in Figure S2. [e] Calculated using group-additivity contributions from Table S12.

As shown in Table 6, the enthalpies of formation calculated using the atomization reaction are systematically more negative than those obtained using the well-balanced reactions. This phenomenon is already known from the literature [20] and, admittedly, the WBR results are preferable for the further thermochemical calculations (see Table 6, column 3). Unfortunately, there are no experimental data on the methoxy-substituted compounds listed in Table 6. Therefore, validation of these theoretical gas-phase enthalpies of formation is required. Such validation can be performed using either the "centrepiece" (CP) approach or conventional group additivity (GA). The contributions required for the application of the CP approach are shown in Figure S2. The contributions required for the application of the GA method are given in Table S12. The results of the empirical calculations using both methods are shown in columns 4 and 5 of Table 6. Admittedly, both empirical methods are not applicable for molecules where the substituents are located in close proximity on the ring (ortho-substituted species in Table 6). However, there is remarkable agreement between the $\Delta_f H_m^o$(g)$_{WBR}$ and $\Delta_f H_m^o$(g)$_{CP}$ results for the meta- and para-substituted biphenyls, benzenes, bicyclohexanes, and cyclohexanes (see comparison of columns 3 and 4 in Table 6). The agreement with the GA method is less satisfactory, especially for the series of methoxy-substituted bicyclohexanes (see comparison of columns 3 and 5 in Table 6). The better predictive performance of the CP approach motivates further development and refinement of this method. In any case, both empirical methods adequately support the $\Delta_f H_m^o$(g)$_{WBR}$ results from quantum chemical calculations. Following, these *theoretical* values $\Delta_f H_m^o$(g, 298.15 K)$_{WBR}$ (see Table 6, column 3) can now be safely combined with the vaporisation enthalpies evaluated in step I (see Table 2) to determine the *theoretical* liquid-phase enthalpies of formation, $\Delta_f H_m^o$(liq, 298.15 K)$_{theor}$, according to Equation (1). The latter values are essential for calculations of energetics of hydrogenation and transfer hydrogenation reactions in the third step.

4.6. Step III: Energetics of Hydrogenation and Transfer Hydrogenation Reactions Based on Methoxy-Biphenyls

The reaction enthalpies in the liquid phase, $\Delta_r H_m^o$(liq), are an important parameter for optimizing the conditions for hydrogen storage using LOHCs. They are usually derived

from the liquid-phase enthalpies of formation of the reactants according to Hess's Law. The $\Delta_f H_m^o$(liq, 298.15 K) values for the participants of the reactions considered in Figure 2 are not known. However, with the enthalpies of vaporisation evaluated in Table 2 and the *theoretical* for the gas-phase enthalpies of formation, $\Delta_f H_m^o$(g, 298.15 K)$_{theor}$, the desired $\Delta_f H_m^o$(liq, 298.15 K)$_{theor}$ values were calculated (see Table 7, column 4) and used for the thermodynamic analysis.

Table 7. Thermochemical data at T = 298.15 K (p° = 0.1 MPa) for methoxy-biphenyls and methoxy-cyclohexanes required to derive the theoretical liquid-phase enthalpies of formation (in kJ·mol^{-1}) [a].

Compound	$\Delta_f H_m^o$(g)$_{WBR}$ [b]	$\Delta_l^g H_m^o$ [c]	$\Delta_f H_m^o$(liq)$_{theor}$ [d]
2-methoxy-biphenyl	32.0	57.8 ± 0.4	−25.8 ± 3.5
3-methoxy-biphenyl	26.0	78.8 ± 1.3	−52.8 ± 3.7
4-methoxy-biphenyl	26.9	79.9 ± 0.9	−53.0 ± 3.6
4,4′-dimethoxy-biphenyl	−125.6	91.9 ± 1.4	−217.5 ± 3.7
methoxy-cyclohexane	−270.7 [e]	43.0 ± 0.5	−313.7 ± 3.5
2-methoxy-bicyclohexane	−362.1	66.1 ± 1.5	−428.2 ± 3.8
3-methoxy-bicyclohexane	−362.2	69.3 ± 1.5	−431.5 ± 3.8
4-methoxy-bicyclohexane	−361.5	69.3 ± 1.5	−430.8 ± 3.8
4,4′-dimethoxy-bicyclohexane	−508.9	79.2 ± 1.5	−588.1 ± 3.8

[a] Uncertainties correspond to expanded uncertainties of the mean (0.95 level of confidence). [b] Calculated in this work according to the well-balanced reactions (see Figure 7). The uncertainties of the G4 method were assessed to be ±3.5 kJ·mol^{-1} [11]. [c] The evaluated values from Table 2. [d] The difference in columns 2 and 3. [e] Calculated via the G4 method using the atomisation reaction.

The enthalpies of reactions hydrogenation/dehydrogenation and transferhydrogenation considered in Figure 2 were derived according to Hess's Law using the standard molar enthalpies of formation of the reactants summarized in Table 7, column 4. The compilation of data required for these calculations and the resulting $\Delta_r H_m^o$(liq) values are shown in Table 8.

Table 8. Calculation of the liquid-phase reaction enthalpies, $\Delta_r H_m^o$(liq), of the hydrogenation of methoxy-biphenyls (Reactions 1 in Figure 2), at T = 298.15 K (p° = 0.1 MPa, in kJ·mol^{-1}).

Compound	$\Delta_f H_m^o$(liq)$_{HL}$ [a]	$\Delta_f H_m^o$(liq)$_{HR}$ [b]	$\Delta_r H_m^o$(liq) [c]	$\Delta_r H_m^o$(liq)/H$_2$ [d]
methoxy-benzene	−116.9 ± 0.7 [e]	−313.7 ± 3.5 [e]	−196.8	−65.6
2-methoxy-biphenyl	−25.8 ± 3.5	−428.2 ± 3.8	−402.4	−67.1
3-methoxy-biphenyl	−52.8 ± 3.7	−431.5 ± 3.8	−378.7	−63.1
4-methoxy-biphenyl	−53.0 ± 3.6	−430.8 ± 3.8	−377.8	−63.0
4,4′-dimethoxy-biphenyl	−217.5 ± 3.7	−588.1 ± 3.8	−370.6	−61.7

[a] Liquid-phase enthalpies of formation of methoxy-biphenyls (hydrogen-lean (HL) counterparts of the LOHC system) from Table 7. [b] Liquid-phase enthalpies of formation of perhydrogenated methoxy-biphenyls (or methoxy-cyclohexanes) from (hydrogen-rich (HR) counterparts of the LOHC system) Table 7. [c] Calculated according to the Hess's Law applied to the Reaction (1) shown in Figure 2. [d] Reaction enthalpy per mole H$_2$. [e] From Table S10.

As shown in Table 8, the hydrogenation of the methoxy-biphenyls is highly exothermic from −371 to −402 kJ·mol^{-1} (see Table 8, column 4), and this energy must be taken into account when optimising the design of chemical reactors. It is convenient to relate the enthalpy of reaction to the amount of hydrogen released (kJ·mol^{-1}/$_{H2}$). This allows a comparison of the reaction enthalpies of LOHC systems with different stoichiometries (see Table 8, column 5). In these units the reaction enthalpies of the methoxy-biphenyls (at −61.7 to −67.1 kJ·mol^{-1}/$_{H2}$) are very similar to those of methoxy-benzene (−65.6 kJ·mol^{-1}/$_{H2}$) or commercially available thermofluids benzyltoluenes and dibenzyltoluenes (−63.5 and −65.4 kJ·mol^{-1}/$_{H2}$), respectively [21].

The enthalpies of TH reactions according to Reactions 2 (see Figure 2) were derived using the standard molar enthalpies of formation of the reactants summarized in in Ta-

ble 7, column 4. The compilation of data required for these calculations and the resulting $\Delta_r H_m^o(\text{liq})$ values are shown in Table 9.

Table 9. Calculation of the liquid-phase reaction enthalpies, $\Delta_r H_m^o(\text{liq})$, of the transfer hydrogenation based on methoxy-cyclohexanes (Reactions 2 in Figure 2), at T = 298.15 K (p° = 0.1 MPa, in kJ·mol^{-1}).

Compound	$\Delta_f H_m^o(\text{liq})_{AC}$ [a]	$\Delta_f H_m^o(\text{liq})_{iPr}$ [b]	$\Delta_f H_m^o(\text{liq})_{HR}$ [c]	$\Delta_f H_m^o(\text{liq})_{HL}$ [d]	$\Delta_r H_m^o(\text{liq})$ [e]
methoxy-cyclohexane	-248.1 ± 0.7	-318.1 ± 0.5	-313.7 ± 3.5	-116.9 ± 0.7	-13.2
2-methoxy-bicyclohexane	-248.1 ± 0.7	-318.1 ± 0.5	-428.2 ± 3.8	-25.8 ± 3.5	-17.6
3-methoxy-bicyclohexane	-248.1 ± 0.7	-318.1 ± 0.5	-431.5 ± 3.8	-52.8 ± 3.7	-41.3
4-methoxy-bicyclohexane	-248.1 ± 0.7	-318.1 ± 0.5	-430.8 ± 3.8	-53.0 ± 3.6	-42.2
4,4'-dimethoxy-bicyclohexane	-248.1 ± 0.7	-318.1 ± 0.5	-588.1 ± 3.8	-217.5 ± 3.7	-49.4

[a] Liquid-phase enthalpy of formation of acetone from Table S10. [b] Liquid-phase enthalpies of formation of iso-propanol from Table S10. [c] Liquid-phase enthalpies of formation of perhydrogenated methoxy-biphenyls (or methoxy-cyclohexanes) from (hydrogen-rich (HR) counterparts of the LOHC system) Table 7. [d] Liquid-phase enthalpies of formation of methoxy-biphenyls (hydrogen-lean (HL) counterparts of the LOHC system) from Table 7. [e] Calculated according to the Hess's Law applied to the Reactions 2 in Figure 2, using liquid-phase enthalpies of formation of acetone and iso-propyl alcohol from Table S10.

As it shown in Table 9, column 6, the TH reactions based on the methoxy-cyclohexanes are significantly less exothermic compared to direct hydrogenation. Such an energetic advantage also speaks to the mild reaction conditions in TH compared to conventional dehydrogenation/hydrogenation processes. Therefore, our ongoing studies on TH reactions with different types of hydrogen acceptors and donors could open up new possibilities for hydrogen storage and utilisation in the future, especially if the donors and acceptors could come from renewable sources.

4.7. Thermodynamic Analysis of the Reversible Hydrogenation/Dehydrogenation Process in the Gas Phase

Admittedly, the dehydrogenation of the hydrogen-rich LOHC counterpart is a thermodynamically unfavourable process [22]. Therefore, proper selection of optimal dehydrogenation temperatures is a direct way to increase hydrogen yield. In our recent work [23], we proposed an approach to evaluate the optimal dehydrogenation temperatures based on quantum chemical calculations of the Gibbs free energy. According to the Gibbs free energy equation,

$$\Delta_r G_m^o(g) = \Delta_r H_m^o(g) - T \times \Delta_r S_m^o(g) \tag{9}$$

at low temperatures the enthalpy term predominates over the entropy term, so that hydrogenation is possible. When $\Delta_r G_m^o = 0$, the enthalpy term $\Delta_r H_m^o$ and the entropy term $T \times \Delta_r S_m^o$ in Equation (9) become equal. This occurs at a certain "equilibrium temperature", T_{eq}, which can imply the reversal of thermodynamic feasibility from hydrogenation to dehydrogenation tendency:

$$T_{\text{eq}} = \frac{\Delta_r H_m^o}{\Delta_r S_m^o}. \tag{10}$$

This temperature should be a valuable indicator for the selection and development of an effective LOHC system. This T_{eq} should not be too low for the hydrogenation step to achieve acceptable reaction rates; the T_{eq} for the dehydrogenation step should not be too high but sufficient to achieve good conversion and selectivity. Results for T_{eq} calculations according to Equation (10) for methoxy-cyclohexanes are compared in Table 10.

As can be seen in Table 10, the T_{eq} values for dehydrogenation in methoxy-substituted LOHC systems vary between 516 and 539 K, depending on the position of the CH$_3$O group on the aliphatic rings. The lowest equilibrium temperature is observed for 4,4'-dimethoxy-bicyclohexane (516 K). However, except for 2-methoxy-bicyclohexane (527 K), the T_{eq} values for all methoxy-substituted species are very close (see Table 10).

Table 10. Thermodynamic analysis of the dehydrogenation of methoxy-cyclohexanes in the gas phase calculated using the G4 method (at 298.15 K and p° = 0.1 MPa).

HR-Counterpart	$\Delta_r G_m^o$	$\Delta_r H_m^o$	$\Delta_r S_m^o$	T_{eq}
methoxy-cyclohexane	−87.3	−195.2	−362.0	539
bicyclohexane	−162.2	−383.2	−741.1	517
2-methoxy-bicyclohexane	−166.7	−384.4	−729.9	527
3-methoxy-bicyclohexane	−160.4	−378.5	−731.4	518
4-methoxy-bicyclohexane	−160.6	−378.6	−731.3	518
4,4′-dimethoxy-bicyclohexane	−158.3	−374.5	−725.2	516

It is interesting to note that the dehydrogenation of 2-methoxy-bicyclohexane occurs with the highest T_{eq} among the methoxy-compounds considered in Table 10, and at the same time the dehydrogenation enthalpy for this compound (of 67.1 kJ·mol^{-1}/$_{H2}$, see Table 10) is also the highest. This observation is important for the proper selection of LOHC systems. Obviously, the ortho-substituted methoxy-substituted aromatic compounds are less suitable for hydrogen storage via reversible hydrogenation/dehydrogenation. In contrast, hydrogen storage via transfer hydrogenation with 2-methoxybicyclohexane is more advantageous by a factor of 1.5 compared to the meta- and para-isomers, since the reaction enthalpy of −17.6 kJ·mol^{-1} is the lowest in this series (see Table 9). These new findings contribute to a better understanding of the reaction thermodynamic properties of LOHC systems and reveal the structural features of aromatic compounds that are essential for their technical applications.

5. Conclusions

Methoxy-substituted biphenyls have been studied thermodynamically regarding their applicability as LOHC materials. The consistent sets of phase transition enthalpies and formation enthalpies were obtained using vapour pressure determinations, thermal behaviour studies, empirical, and quantum chemical calculations. These results were recommended for chemical engineering calculations to optimize reversible reactions for the storage and release of hydrogen. The reaction enthalpies of hydrogenation of methoxy-biphenyls in the liquid phase were calculated and compared with other types of hydrogen carriers. Generally, a reduction in enthalpy of reaction for the dehydrogenation reaction is desired to achieve more beneficial reaction conditions. The hydrogenation enthalpies were found to be of the same order of magnitude as for the common aromatic compounds. The results show that substitution with methoxy groups on the ring can have a positive effect on the reaction thermodynamics. However, the effect is dependent on the position of the substitution. The meta- and para- substitution of the aromatic ring increases the positive effect of the introduction of the methoxy group. The "equilibrium temperatures" of the meta- and para-methoxy-substituted compounds are significantly lower compared to those of the ortho-substituted isomers. The energetics of the TH reaction based on the methoxy-cyclohexanes was also calculated and proved to be significantly less exothermic compared to direct hydrogenation. The results of this study may contribute to a better understanding of the reaction thermodynamics of potential LOHC materials and their chemical structure. However, from a technical point of view, it is important to consider that the appending of an ether functionality to a LOHC compound introduces some risk of ether cleavage during the catalytic hydrogenation step that loads the LOHC compound with hydrogen. This issue needs to be addressed in catalyst development studies. The thermodynamic analysis presented here shows that such an approach could be very rewarding to provide promising LOHC systems for efficient hydrogen release in mild temperature conditions.

vaporisation enthalpies, and entropies obtained using the approximation of boiling points at different pressures available in the literature; Table S4. Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$ (298.15 K), of alkoxy-substituted aromatics with their Kovats indices (J_x); Table S5. Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$ (298.15 K), of alkoxy-substituted aromatics with their Kovats indices (J_x); Table S6: Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$ (298.15 K), of diakyl ethers with their Kovats indices (Jx); Table S7: Correlation of the normal boiling temperatures, T_b, of dialkyl ethers with their J_x (retention indices); Table S8: Enthalpies of fusion ($\Delta_{cr}^l H_m^o$), vaporisation ($\Delta_l^g H_m^o$), and sublimation ($\Delta_{cr}^g H_m^o$) of auxiliary compounds at melting points (T_{fus}) and 298 K (in kJ·mol^{-1}); Table S9: Correlation of vapor-isation enthalpies, $\Delta_l^g H_m^o$ (298.15 K), of substituted phenols with their Kovats indices (J_x); Table S10: Thermochemical data at T = 298.15 K (p° = 0.1 MPa) for reference compounds (in kJ·mol^{-1}); Table S11: Correlation of the normal boiling temperatures, T_b, of dialkyl ethers with the standard molar en-thalpies of vaporisation, $\Delta_l^g H_m^o$ (298.15 K); Table S12: Group-additivity values Γ_i for calculation of enthalpies of vaporisation, $\Delta_l^g H_m^o$, and enthalpies of formation, $\Delta_f H_m^o$(g), of alkanes, ethers, and aromatics at 298.15 K in kJ mol^{-1}; Table S13: Structures of the most stable conformers and the G4 calculated gas-phase enthalpies of formation $\Delta_f H_m^o$(g)$_{G4}$ at T = 298.15 K (p° = 0.1 MPa) for methoxy-bicyclohexyls (in kJ·mol^{-1}); Figure S1: Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$ (298.15 K), of hydroxy-iso-propylbenzenes and methoxy-iso-propylbenzenes; Figure S2: The development of the contributions for calculating the vaporisation enthalpies (or gas-phase enthalpies of formation) of aromatic and cyclic aliphatic hydrocarbons using the "centerpiece" approach. The auxiliary experi-mental and computational details necessary to understand the main points of the paper are given in Refs. [24–56].

Data Availability Statement: Not applicable.

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

References

1. Zaitsau, D.H.; Emel'yanenko, V.N.; Pimerzin, A.A.; Verevkin, S.P. Benchmark properties of biphenyl as a liquid organic hydrogen carrier: Evaluation of thermochemical data with complementary experimental and computational methods. *J. Chem. Thermodyn.* **2018**, *122*, 1–12. [CrossRef]
2. Zhang, H.; Zhang, X.; Shi, S.; He, Q.; He, X.; Gan, T.; Ji, H. Highly Efficient Fabrication of Kilogram-Scale Palladium Single-Atom Catalysts for the Suzuki–Miyaura Cross-Coupling Reaction. *ACS Appl. Mater. Interfaces* **2022**, *14*, 53755–53760. [CrossRef] [PubMed]
3. Chen, K.; He, G.; Tang, Q. Air and moisture stable robust bio-polymeric palladium catalyzed C C bond formation and its application to the synthesis of fungicidal. *J. Ind. Eng. Chem.* **2023**, *124*, 165–174. [CrossRef]
4. Sun, Z.; Duan, L.; Huang, C.; Wu, B. Preparation of Biphenyl Derivatives by Using Magnetic Ctalyst in Liquid-Solid Reaction China. CN116143573 A 23 May 2023.
5. Gelis, C.; Heusler, A.; Nairoukh, Z.; Glorius, F. Catalytic Transfer Hydrogenation of Arenes and Heteroarenes. *Chem.-A Eur. J.* **2020**, *26*, 14090–14094. [CrossRef]
6. Sievi, G.; Geburtig, D.; Skeledzic, T.; Bösmann, A.; Preuster, P.; Brummel, O.; Waidhas, F.; Montero, M.A.; Khanipour, P.; Katsounaros, I.; et al. Towards an efficient liquid organic hydrogen carrier fuel cell concept. *Energy Environ. Sci.* **2019**, *12*, 2305–2314. [CrossRef]
7. Zakgeym, D.; Engl, T.; Mahayni, Y.; Müller, K.; Wolf, M.; Wasserscheid, P. Development of an efficient Pt/SiO$_2$ catalyst for the transfer hydrogenation from perhydro-dibenzyltoluene to acetone. *Appl. Catal. A Gen.* **2022**, *639*, 118644. [CrossRef]

8. Zakgeym, D.; Hofmann, J.D.; Maurer, L.A.; Auer, F.; Müller, K.; Wolf, M.; Wasserscheid, P. Better through oxygen functionality? The benzophenone/dicyclohexylmethanol LOHC-system. *Sustain. Energy Fuels* **2023**, *7*, 1213–1222. [CrossRef]

9. Peterson, K.A.; Feller, D.; Dixon, D.A. Chemical accuracy in ab initio thermochemistry and spectroscopy: Current strategies and future challenges. *Theor. Chem. Acc.* **2012**, *131*, 1079. [CrossRef]

10. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; et al. *Gaussian 16, Revision C.01*; Gaussian, Inc.: Wallingford, CT, USA, 2016.

11. Curtiss, L.A.; Redfern, P.C.; Raghavachari, K. Gaussian-4 theory. *J. Chem. Phys.* **2007**, *126*, 084108. [CrossRef]

12. Samarov, A.A.; Verevkin, S.P. Comprehensive thermodynamic study of alkyl-biphenyls as a promising Liquid Organic Hydrogen Carriers. *J. Chem. Thermodyn.* **2022**, *174*, 106872. [CrossRef]

13. Kováts, E. Gas-chromatographische Charakterisierung organischer Verbindungen. Teil 1: Retentionsindices aliphatischer Halogenide, Alkohole, Aldehyde und Ketone. *Helv. Chim. Acta* **1958**, *41*, 1915–1932. [CrossRef]

14. Okumura, T. Retention Indices of Environmental Chemicals on Methyl Silicone Capillary Column. *J. Environ. Chem.* **1991**, *1*, 333–358. [CrossRef]

15. Verevkin, S.P.; Konnova, M.E.; Turovtsev, V.V.; Riabchunova, A.V.; Pimerzin, A.A. Weaving a Network of Reliable Thermochemistry around Lignin Building Blocks: Methoxy-Phenols and Methoxy-Benzaldehydes. *Ind. Eng. Chem. Res.* **2020**, *59*, 22626–22639. [CrossRef]

16. Benson, S.W. *Thermochemical Kinetics*, 2nd ed.; John Wiley & Sons: Hoboken, NJ, USA, 1976; pp. 1–320.

17. Verevkin, S.P.; Andreeva, I.V.; Zherikova, K.V.; Pimerzin, A.A. Prediction of thermodynamic properties: Centerpiece approach—How do we avoid confusion and get reliable results? *J. Therm. Anal. Calorim.* **2022**, *147*, 8525–8534. [CrossRef]

18. Pracht, P.; Bohle, F.; Grimme, S. Automated exploration of the low-energy chemical space with fast quantum chemical methods. *Phys. Chem. Chem. Phys.* **2020**, *22*, 7169–7192. [CrossRef]

19. Petersson, G.A.; Bennett, A.; Tensfeldt, T.G.; Al-Laham, M.A.; Shirley, W.A.; Mantzaris, J. A complete basis set model chemistry. I. The total energies of closed-shell atoms and hydrides of the first-row elements. *J. Chem. Phys.* **1988**, *89*, 2193–2218. [CrossRef]

20. Wheeler, S.E.; Houk, K.N.; Schleyer, P.v.R.; Allen, W.D. A Hierarchy of Homodesmotic Reactions for Thermochemistry. *J. Am. Chem. Soc.* **2009**, *131*, 2547–2560. [CrossRef]

21. Müller, K.; Stark, K.; Emel'yanenko, V.N.; Varfolomeev, M.A.; Zaitsau, D.H.; Shoifet, E.; Schick, C.; Verevkin, S.P.; Arlt, W. Liquid Organic Hydrogen Carriers: Thermophysical and Thermochemical Studies of Benzyl- and Dibenzyl-toluene Derivatives. *Ind. Eng. Chem. Res.* **2015**, *54*, 7967–7976. [CrossRef]

22. Müller, K.; Völkl, J.; Arlt, W. Thermodynamic Evaluation of Potential Organic Hydrogen Carriers. *Energy Technol.* **2013**, *1*, 20–24. [CrossRef]

23. Verevkin, S.P.; Emel'yanenko, V.N.; Siewert, R.; Pimerzin, A.A. Energetics of LOHC: Structure-Property Relationships from Network of Thermochemical Experiments and in Silico Methods. *Hydrogen* **2021**, *2*, 101–121. [CrossRef]

24. Kulikov, D.; Verevkin, S.P.; Heintz, A. Determination of Vapor Pressures and Vaporization Enthalpies of the Aliphatic Branched C 5 and C 6 Alcohols. *J. Chem. Eng. Data* **2001**, *46*, 1593–1600. [CrossRef]

25. Verevkin, S.P.; Emel'yanenko, V.N. Transpiration method: Vapor pressures and enthalpies of vaporization of some low-boiling esters. *Fluid Phase Equilib.* **2008**, *266*, 64–75. [CrossRef]

26. Verevkin, S.P.; Sazonova, A.Y.; Emel'yanenko, V.N.; Zaitsau, D.H.; Varfolomeev, M.A.; Solomonov, B.N.; Zherikova, K.V. Thermochemistry of Halogen-Substituted Methylbenzenes. *J. Chem. Eng. Data* **2015**, *60*, 89–103. [CrossRef]

27. Emel'yanenko, V.N.; Verevkin, S.P. Benchmark thermodynamic properties of 1,3-propanediol: Comprehensive experimental and theoretical study. *J. Chem. Thermodyn.* **2015**, *85*, 111–119. [CrossRef]

28. Emel'yanenko, V.N.; Zaitsau, D.H.; Shoifet, E.; Meurer, F.; Verevkin, S.P.; Schick, C.; Held, C. Benchmark Thermochemistry for Biologically Relevant Adenine and Cytosine. A Combined Experimental and Theoretical Study. *J. Phys. Chem. A* **2015**, *119*, 9680–9691. [CrossRef]

29. Chickos, J.S.; Hosseini, S.; Hesse, D.G.; Liebman, J.F. Heat capacity corrections to a standard state: A comparison of new and some literature methods for organic liquids and solids. *Struct. Chem.* **1993**, *4*, 271–278. [CrossRef]

30. Chickos, J.S.; Acree, W.E. Enthalpies of Vaporization of Organic and Organometallic Compounds, 1880–2002. J. *Phys. Chem. Ref. Data* **2003**, *32*, 519–878. [CrossRef]

31. Verevkin, S.P. Weaving a web of reliable thermochemistry around lignin building blocks: Phenol, benzaldehyde, and anisole. *J. Therm. Anal. Calorim.* **2022**, *147*, 6073–6085. [CrossRef]

32. SciFinder—Chemical Abstracts Service. Available online: http://scifinder.cas.org/ (accessed on 24 April 2023).

33. Reaxys. Available online: https://www.reaxys.com/ (accessed on 24 April 2023).

34. Guidechem Chemical Network. Available online: https://www.guidechem.com (accessed on 24 April 2023).

35. Majer, V.; Svoboda, V. *Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation*; Blackwell Scientific Publications: Oxford, UK, 1985.

36. Emel'yanenko, V.N.; Zaitseva, K.V.; Agapito, F.; Martinho Simões, J.A.; Verevkin, S.P. Benchmark thermodynamic properties of methylanisoles: Experimental and theoretical study. *J. Chem. Thermodyn.* **2015**, *85*, 155–162. [CrossRef]

37. Dreisbach, R.R.; Martin, R.A. Physical Data on Some Organic Compounds. *Ind. Eng. Chem.* **1949**, *41*, 2875–2878. [CrossRef]

38. Stull, D.R. Vapor Pressure of Pure Substances. Organic and Inorganic Compounds. *Ind. Eng. Chem.* **1947**, *39*, 517–540. [CrossRef]

39. Tsuge, S.; Ohtani, H.; Watanabe, C. *Pyrolysis—GC/MS Data Book of Synthetic Polymers*; Elsevier: Amsterdam, The Netherlands, 2011.

40. Efimova, A.A.; Druzhinina, A.I.; Varushchenko, R.M.; Dorofeeva, O.V.; Krasnyh, E.L. Phase Equilibria and Thermodynamic Properties of Some Branched Alkyl Ethers. *J. Chem. Eng. Data* **2009**, *54*, 2457–2469. [CrossRef]

41. NIST Chemistry WebBook. Available online: https://webbook.nist.gov/chemistry/ (accessed on 30 August 2023).

42. Verevkin, S.P. Determination of the ortho -, para -, and meta -Interactions in secondary -Alkylphenols from Thermochemical Measurements. Berichte der Bunsengesellschaft für Phys. *Chemie* **1998**, *102*, 1467–1473. [CrossRef]

43. Verevkin, S.P. Thermochemistry of phenols: Experimental standard molar enthalpies of formation of 2-phenylphenol, 4-phenylphenol, 2,6-diphenylphenol, and 2,2′- and 4,4′-dihydroxybiphenyl. *J. Chem. Thermodyn.* **1998**, *30*, 389–396. [CrossRef]

44. Bertholon, G.; Giray, M.; Perrin, R.; Vincent-Falquet-Berny, M.F. No. 532.—Etude physicochimique des phenols. OX.—Ethanlpies de combustion et energies de resonance des alcoyl et aryphenols. *Bull. Soc. Chim. Fr.* **1971**, 3180–3187.

45. Abdelaziz, A.; Zaitsau, D.H.; Kuratieva, N.V.; Verevkin, S.P.; Schick, C. Melting of nucleobases. Getting the cutting edge of "Walden's Rule.". *Phys. Chem. Chem. Phys.* **2019**, *21*, 12787–12797. [CrossRef]

46. Walden, P. Über die Schmelzwärme, spezifische Kohäsion und Molekulargrösse bei der Schmelztemperatur. *Z. Für Elektrotechnik Und Elektrochem.* **1908**, *14*, 713–724. [CrossRef]

47. Chickos, J.S.; Hesse, D.G.; Liebman, J.F. Estimating Enthalpies of Sublimation of Hydrocarbons. In *Energetics of Organometallic Species*; Springer: Dordrecht, The Netherlands, 1992.

48. Nagrimanov, R.N.; Ziganshin, M.A.; Solomonov, B.N.; Verevkin, S.P. Thermochemistry of drugs: Experimental and theoretical study of analgesics. *Struct. Chem.* **2019**, *30*, 247–261. [CrossRef]

49. Roux, M.V.; Temprado, M.; Chickos, J.S.; Nagano, Y. Critically evaluated thermochemical properties of polycyclic aromatic hydrocarbons. *J. Phys. Chem. Ref. Data* **2008**, *37*, 1855–1996. [CrossRef]

50. Pedley, J.B.; Naylor, R.D.; Kirby, S.P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: New York, NY, USA, 1986; pp. 1–792.

51. Konnova, M.E.; Vostrikov, S.V.; Pimerzin, A.A.; Verevkin, S.P. Thermodynamic analysis of hydrogen storage: Biphenyl as affordable liquid organic hydrogen carrier (LOHC). *J. Chem. Thermodyn.* **2021**, *159*, 106455. [CrossRef]

52. Mokbel, I.; Rauzy, E.; Loiseleur, H.; Berro, C.; Jose, J. Vapor pressures of 12 alkylcyclohexanes, cyclopentane, butylcyclopentane and trans-decahydronaphthalene down to 0.5 Pa. Experimental results, correlation and prediction by an equation of state. *Fluid Phase Equilib.* **1995**, *108*, 103–120. [CrossRef]

53. Hückel, W.; Bross, R.; Fechtig, O.; Feltkamp, H.; Geiger, S.; Hanack, M.; Heinzel, M.; Hubele, A.; Kurz, J.; Maier, M.; et al. Beiträge zur Konstellationsanalyse, III Alkoholyse von Toluolsulfonsäureestern, V. *Justus Liebigs Ann. Chem.* **1959**, *624*, 142–255. [CrossRef]

54. Ducros, M.; Gruson, J.F.; Sannier, H. Estimation des enthalpies de vaporisation des composes organiques liquides. Partie 1. Applications aux alcanes, cycloalcanes, alcenes, hydrocarbures benzeniques, alcools, alcanes thiols, chloro et bromoalcanes, nitriles, esters, acides et aldehydes. *Thermochim. Acta* **1980**, *36*, 39–65. [CrossRef]

55. Ducros, M.; Gruson, J.F.; Sannier, H.; Velasco, I. Estimation des enthalpies de vaporisation des composes organiques liquides. Partie 2. Applications aux ethersoxydes, thioalcanes, cetones et amines. *Thermochim. Acta* **1981**, *44*, 131–140. [CrossRef]

56. Verevkin, S.P.; Beckhaus, H.-D.; Belen'kaja, R.S.; Rakus, K.; Rüchardt, C. Geminal substituent effects Part 9. Standard enthalpies of formation and strain free increments of branched esters and ethers. *Thermochim. Acta* **1996**, *279*, 47–64. [CrossRef]