

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

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Materials

The samples of methoxy-biphenyls used in this work were of commercial origin (see Table S1). The sample of 2-methoxy-biphenyl was purified by fractional distillation under reduced pressure. The samples of 4-methoxy-biphenyl and 4,4'-dimethoxy-biphenyl were purified by fractional sublimation under reduced pressure. 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 $0.167 \text{ K} \cdot \text{s}^{-1}$ to $T = 573$ K. No impurities (greater than 0.0002 mass fraction) were detected in samples used for thermochemical measurements.

Table S1. Provenance and purity of the materials

Material ^a	CAS	Origin	Initial GC purity (mass fraction)	GC purity after purification (mass fraction)
2-methoxybiphenyl (liq)	86-26-0	TCI	0.9982	0.9999 ^a
4-methoxybiphenyl (cr)	613-37-6	TCI	0.9990	0.9998 ^b
4,4'-dimethoxybiphenyl (cr)	613-33-2	Sigma	0.9931	0.9998 ^b

^a Sample was additionally purified using fractional distillation and used for transpiration measurements.

^b Sample was additionally purified using fractional sublimation and used for DSC and transpiration measurements.

Transpiration method: Vapour pressure measurements

Absolute vapour pressures were measured using the transpiration method [1,2]. 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 (± 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:

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

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. The standard uncertainties for T , V , p , m , are standard uncertainties with 0.683 confidence levels.

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.

Standard uncertainties of vapor pressures were calculated with $u(p_i/\text{Pa}) = 0.005 + 0.025(p_i/\text{Pa})$ for pressures below 5 Pa, and $u(p_i/\text{Pa}) = 0.025 + 0.025(p_i/\text{Pa})$ for pressures from 5 to 3000 Pa. Uncertainty of the sublimation/vaporisation enthalpy $U(\Delta_{cr,l}^g H_m^o)$ is the expanded uncertainty (0.95 level of confidence) calculated according to procedure described elsewhere [3,4].

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 [3,4]. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapour pressures, and uncertainties from adjustment of vaporisation enthalpies to the reference temperature $T = 298.15$ K.

The uncertainties of the $\Delta_l^g H_m^o(298.15 \text{ K})$ -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.

Differential scanning calorimetry: thermal behavior and fusion enthalpies

The thermal behavior of crystalline sample of methoxy-biphenyls including melting temperature and enthalpy of fusion was studied with a commercial DSC Mettler Toledo DSC 822e coupled with Huber TC100MT cooler [5]. The sample was placed in the standard non-pinned aluminium pan. The pan and sample were weighed with the Sartorius MSE3.6P-000-DM microbalance with the standard uncertainty of $5 \cdot 10^{-6}$ g. The calibration of the DSC was checked with melting behaviour of reference indium sample. The temperature of fusion agreed with the recommended value better than 0.3 K. For the enthalpy of fusion the maximum deviation from the recommended value was at the level of $0.2 \text{ kJ} \cdot \text{mol}^{-1}$. In the first DSC run the sample was heated with a rate $10 \text{ K} \cdot \text{min}^{-1}$ to 398 K (~ 30 K above melting temperature provided by supplier) and then cooled down to 298 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.

Adjustment of vaporisation/sublimation/fusion enthalpies to the reference temperature $T = 298.18 \text{ K}$

The standard molar enthalpies of vaporization/sublimation of methoxy-biphenyls at temperatures T were derived from the temperature dependence of the vapor pressures, approximated by Eq. (S1) using the following equation:

$$\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\text{o}}(T) = -b + \Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\text{o}} \times T \quad (\text{S2})$$

where b is one of the adjustable parameters of Eq. (S1). The standard molar vaporization/sublimation entropies at temperatures T were also derived from the temperature dependences of the vapor pressures (approximated by Eq. S1) as follows:

$$\Delta_{\text{cr,l}}^{\text{g}} S_{\text{m}}^{\text{o}}(T) = \Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\text{o}}/T + R \times \ln(p_i/p^{\text{o}}) \quad (\text{S3})$$

with $p^{\text{o}} = 0.1$ MPa. According to common practice, the comparison of thermochemical results is usually carried out at the reference temperature $T = 298.15$ K.

The general thermochemical equation:

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}} = \Delta_{\text{l}}^{\text{g}} H_{\text{m}}^{\text{o}} + \Delta_{\text{cr}}^{\text{l}} H_{\text{m}}^{\text{o}} \quad (\text{S4}),$$

connects the phase change enthalpies and it can be used to establish an internal consistency of the experimental data on the experimental sublimation (Table 2), fusion (Table 3), and vaporization enthalpies (Table 2). It is important that all enthalpies involved in Eq. (S4) are referenced to the same temperature, *e.g.* to the reference temperature $T = 298.15$ K. However, the enthalpies of fusion results given in Table 3 are ascribed to the melting temperature. These data must be adjusted to the reference temperature $T = 298.15$ K for the thermochemical calculations. For this purpose, we used the well-established general procedure [6,7] based on the Kirchhoff equation, *e.g.* for the sublimation enthalpy:

$$\Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(298.15 \text{ K}) \text{ } / (\text{J} \cdot \text{mol}^{-1}) = \Delta_{\text{cr}}^{\text{g}} H_{\text{m}}^{\text{o}}(T_{\text{av}}/\text{K}) - (C_{\text{p,m}}^{\text{o}}(\text{cr}) - C_{\text{p,m}}^{\text{o}}(\text{liq})) \times [(T_{\text{av}}/\text{K}) - 298.15 \text{ K}] \quad (\text{S5})$$

where $C_{\text{p,m}}^{\text{o}}(\text{cr})$ and $C_{\text{p,m}}^{\text{o}}(\text{liq})$ are the isobaric molar heat capacities (given in Table S2).

The sublimation/vaporisation enthalpies, which are derived from the experimental vapor pressure-temperature dependencies according to the Clausius–Clapeyron relation, are referenced to the average temperature, T_{av} , of the examined interval. For engineering calculations, these enthalpies should be adjusted to the reference temperature $T = 298.15$ K. The enthalpies of sublimation/vaporisation are derived using the following equation:

$$\Delta_{\text{cr,l}}^{\text{g}} H_{\text{m}}^{\text{o}}(T) = -b + \Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\text{o}} \times T \quad (\text{S6})$$

The $\Delta_{\text{cr,l}}^{\text{g}} C_{\text{p,m}}^{\text{o}}$ -values used in Eq. (S6) are usually derived according to empirical equations developed by Chickos and Acree [6,7]:

$$\Delta_{\text{l}}^{\text{g}} C_{\text{p,m}}^{\text{o}}(298.15 \text{ K}) = -0.26 \times C_{\text{p,m}}^{\text{o}}(\text{liq}, 298.15 \text{ K}) - 10.58 \quad (\text{S7})$$

$$\Delta_{\text{cr}}^{\text{g}} C_{\text{p,m}}^{\text{o}}(298.15 \text{ K}) = -0.15 \times C_{\text{p,m}}^{\text{o}}(\text{cr}, 298.15 \text{ K}) - 0.75 \quad (\text{S8})$$

where $C_{\text{p,m}}^{\text{o}}(\text{cr}, 298.15 \text{ K})$ or $C_{\text{p,m}}^{\text{o}}(\text{liq}, 298.15 \text{ K})$ values are of experimental origin or they can be also estimated according to the group-additivity procedure [6,7]. For calculations with methoxy-substituted compounds we used the modified Eq. (7)

$$\Delta_{\text{l}}^{\text{g}} C_{\text{p,m}}^{\text{o}}(298.15 \text{ K}) = -0.181 \times C_{\text{p,m}}^{\text{o}}(\text{liq}, 298.15 \text{ K}) - 10.58 \quad (\text{S9})$$

which was developed in our recent work based on the evaluated data for methoxy-benzene [8].

According to common practice, the experimental, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}(T_{\text{fus}})$ -values must also be adjusted to $T = 298.15$ K using Eq. (10) [6,7]:

$$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}(298.15 \text{ K})/(\text{J}\cdot\text{mol}^{-1}) = \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}(T_{\text{fus}}/\text{K}) - (\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\text{o}} - \Delta_{\text{l}}^{\text{g}}C_{\text{p,m}}^{\text{o}}) \times [(T_{\text{fus}}/\text{K}) - 298.15 \text{ K}] \quad (\text{S10})$$

The values of $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\text{o}}$ and $\Delta_{\text{l}}^{\text{g}}C_{\text{p,m}}^{\text{o}}$ are listed in the Table S2. The enthalpies of fusion, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}(298.15 \text{ K})$, estimated with Eq. (10) are given in Table 3, column 4. These values can now be used to establish consistency of the phase transitions for methoxy-biphenyls collected in Table 2 as follows:

$$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = \Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) + \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) \quad (\text{S11})$$

when all enthalpies are adjusted to the common temperature $T = 298.15$ K.

Table S2

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

Compounds	$C_{\text{p,m}}^{\text{o}}(\text{liq})^{\text{a}}$	$-\Delta_{\text{l}}^{\text{g}}C_{\text{p,m}}^{\text{o}}^{\text{b}}$	$C_{\text{p,m}}^{\text{o}}(\text{cr})^{\text{a}}$	$-\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\text{o}}^{\text{c}}$
methoxy-biphenyl	305.0	65.8	238.1	36.5
methoxy-bicyclohexane	357.8	75.3		
di-methoxy-biphenyl	361.4	76.0	284.2	43.4
di-methoxy-bicyclohexane	415.4	85.8		
methoxy-iso-propyl-benzene	272.9	60.0		
iso-propyl-phenol	284.9	84.7	192.4	29.6
phenyl-phenol	317.0	93.0	206.2	31.7
methoxy-cyclohexane	213.0	49.1		

^a The $C_{\text{p,m}}^{\text{o}}(\text{liq})$ -values were calculated according to group-additivity procedure developed by Chickos *et al.* [6,7].

^b Calculated according to empirical equation Eq. (S9).

^c Calculated according to empirical equation Eq. (S8).

Table S3

The vapor pressures p , and standard molar vaporization enthalpies and entropies obtained by the approximation of boiling points at different pressures available in the literature [9–11].

T/K^{a}	p/Pa	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{l}}^{\text{g}}S_{\text{m}}^{\text{o}}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
4-methoxy-biphenyl; $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = (76.5 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$			
$\ln(p/p_{\text{ref}}) = \frac{306.2}{R} - \frac{96129.8}{RT} - \frac{65.8}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$			
430	1333	67.8	121.9
447	2533	66.7	118.7
453	2266	66.3	114.9
573	101325	58.4	102.1

3-methoxy-biphenyl; $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = (77.1 \pm 2.7) \text{ kJ}\cdot\text{mol}^{-1}$

	$\ln (p/p_{\text{ref}}) = \frac{308.3}{R} - \frac{96735.3}{RT} - \frac{65.8}{R} \ln \frac{T}{298.15} ; p_{\text{ref}} = 1 \text{ Pa}$		
358	27	73.2	136.0
359	27	73.1	135.2
393	200	70.9	128.7
396	200	70.7	126.8
399	200	70.5	125.0
413	667	69.6	126.8
566	101325	59.5	105.1
4,4'-di-methoxy-biphenyl; $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = (92.4 \pm 3.2) \text{ kJ} \cdot \text{mol}^{-1}$			
	$\ln (p/p_{\text{ref}}) = \frac{337.8}{R} - \frac{114836.0}{RT} - \frac{75.3}{R} \ln \frac{T}{298.15} ; p_{\text{ref}} = 1 \text{ Pa}$		
388	13	85.6	146.5
403	40	84.5	144.6
438	267	81.9	137.6
611	101325	68.8	112.6
2-methoxy-iso-propyl-benzene; $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = (50.9 \pm 3.8) \text{ kJ} \cdot \text{mol}^{-1}$			
	$\ln (p/p_{\text{ref}}) = \frac{267.8}{R} - \frac{68743.1}{RT} - \frac{60.0}{R} \ln \frac{T}{298.15} ; p_{\text{ref}} = 1 \text{ Pa}$		
307	267	50.3	114.4
308	267	50.2	113.7
353	1733	47.6	101.0
366	2400	46.8	96.8
367	2400	46.7	96.3
368	2400	46.7	95.8
368	2400	46.7	95.8
471	101325	40.5	86.1
471	97325	40.5	85.7
471	101325	40.5	86.1
473	97325	40.4	85.1
473	101325	40.4	85.4
474	101325	40.3	85.1
3-methoxy-iso-propyl-benzene; $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = (56.6 \pm 2.6) \text{ kJ} \cdot \text{mol}^{-1}$			
	$\ln (p/p_{\text{ref}}) = \frac{279.2}{R} - \frac{74528.2}{RT} - \frac{60.0}{R} \ln \frac{T}{298.15} ; p_{\text{ref}} = 1 \text{ Pa}$		
332	400	54.6	118.6
360	1733	52.9	113.3
363	1600	52.7	110.9
364	1600	52.7	110.4
366	2133	52.6	111.6
366	1600	52.6	109.2
368	2133	52.4	110.5
476	98125	46.0	96.6
483	101325	45.5	94.4
484	101325	45.5	94.1
4-methoxy-iso-propyl-benzene; $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15 \text{ K}) = (57.6 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$			
	$\ln (p/p_{\text{ref}}) = \frac{280.9}{R} - \frac{75489.5}{RT} - \frac{60.0}{R} \ln \frac{T}{298.15} ; p_{\text{ref}} = 1 \text{ Pa}$		
331	267	55.6	118.8
332	200	55.6	115.7
332	213	55.6	116.2
345	400	54.8	112.9
355	1333	54.2	116.7
358	1333	54.0	115.0

359	1733	53.9	116.6
368	2533	53.4	114.6
369	2533	53.3	114.0
373	2933	53.1	113.0
389	5999	52.1	110.7
390	5999	52.1	110.2
481	97058	46.7	96.9
481	97058	46.6	96.7
483	101325	46.5	96.4
483	101325	46.5	96.4
483	101991	46.5	96.5
484	101325	46.4	96.1
485	101325	46.4	95.8
485	97325	46.4	95.4
485	100791	46.4	95.7
486	101991	46.3	95.5
486	100791	46.3	95.4
487	101325	46.3	95.1
487	97325	46.3	94.8
488	101325	46.2	94.8

methoxy-cyclohexane; $\Delta_1^g H_m^o(298.15 \text{ K}) = (42.7 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$

$$\ln(p/p_{\text{ref}}) = \frac{252.2}{R} - \frac{57363.5}{RT} - \frac{49.1}{R} \ln \frac{T}{298.15}; p_{\text{ref}} = 1 \text{ Pa}$$

308	1467	42.2	102.0
325	5600	41.4	103.4
333	8533	41.0	102.7
334	8533	41.0	102.2
338	15999	40.8	105.4
403	95992	37.6	92.9
404	101325	37.5	93.0
404	95992	37.5	92.5
405	101325	37.5	92.6
405	101325	37.5	92.6
405	101325	37.5	92.6
406	101325	37.4	92.3
406	101325	37.4	92.3
406	101325	37.4	92.3
406	101325	37.4	92.2
406	101325	37.4	92.2
406	101325	37.4	92.2
407	101591	37.4	92.1
407	101325	37.4	92.0
407	101325	37.4	92.0
407	101325	37.4	92.0
408	101325	37.4	91.8
408	101325	37.3	91.6
408	101325	37.3	91.6
408	101325	37.3	91.6
408	100391	37.3	91.5
409	101325	37.3	91.3
409	101325	37.3	91.3
409	101325	37.3	91.3

^a Uncertainties of the vaporization enthalpies are expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$). They include uncertainties from the fitting equation, and uncertainties from temperature adjustment to $T = 298.15$ K. Uncertainties in the temperature adjustment of vaporization enthalpies to the reference temperature $T = 298.15$ K are estimated to account with 20 % to the total adjustment.

Table S4. Correlation of vaporisation enthalpies, $\Delta_f^g H_m^o(298.15 \text{ K})$, of alkoxy-substituted aromatics with their Kovats indices (J_x)

CAS	Compound	J_x^a	$\Delta_f^g H_m^o(298.15 \text{ K})_{\text{exp}}$	$\Delta_f^g H_m^o(298.15 \text{ K})_{\text{calc}}^b$	^c
		K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
100-66-3	methoxy-benzene	894	46.4±0.2 [8]	46.6	-0.2
2113-56-6	3-MeO-biphenyl	1606	-	79.3	
613-37-6	4-MeO-biphenyl	1606	79.9±0.9 [Table 2]	79.3	0.6
6380-20-7	1-MeO-3-iso-propylbenzene	1149	56.6±2.6 [Table S3]	58.3	-1.7
4132-48-3	1-MeO-4-iso-propylbenzene	1159	57.6±2.1 [Table S3]	58.8	-1.2
103-73-1	ethoxy-benzene	971	51.0±0.2 [12]	50.2	0.8
100-84-5	3-MeO-methylbenzene	1001	52.8±0.5 [13]	51.5	1.3
104-93-8	4-MeO-methylbenzene	1001	53.3±0.4 [13]	51.5	1.8
92-52-4	biphenyl	1342	65.8±0.2 [14]	67.2	-1.4
1126-79-0	n-butyl phenyl ether	1164	59.4±2.5 [15]	59.0	0.4
622-85-5	n-propyl phenyl ether	1065	54.3±2.1 [15]	54.5	-0.2
1515-95-3	4-MeO-ethylbenzene	1091	54.5±1.7 [16]	55.7	-1.2
10568-38-4	3-MeO-ethylbenzene	1080	54.4±1.7 [16]	55.2	-0.8
2132-80-1	4,4-diMeO-biphenyl	1879 ^d	92.4±3.2 [Table S3]	91.8	0.6
150-78-7	1,4-diMeO-benzene	1199	61.6±0.2 [17]	60.6	1.0
151-10-0	1,3-diMeO-benzene	1153	59.7±0.2 [17]	58.5	1.2

^a Kovats indices, J_x , on the non-polar column Ultra 1 from [18].

^b Calculated using equation $\Delta_f^g H_m^o(298.15 \text{ K}) = 5.6 + 0.0459 \times J_x$ with $R^2 = 0.9914$, with the assessed expanded uncertainty of $\pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$ (0.95 level of confidence, $k = 2$).

^c Difference between column 4 and 5 in this table.

^d The Kovats index $J_x = 1965$ measured on Ultra-ALLOY-5 [19] column was recalculated to the Kovats index $J_x = 1879$ on the column Ultra 1, common for other entries in this table.

Table S5. Correlation of vaporisation enthalpies, $\Delta_f^g H_m^o(298.15 \text{ K})$, of 2-alkoxy-substituted aromatics with their Kovats indices (J_x)

CAS	Compound	J_x^a	$\Delta_f^g H_m^o(298.15 \text{ K})_{\text{exp}}$	$\Delta_f^g H_m^o(298.15 \text{ K})_{\text{calc}}^b$	^c
		K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
103754-94-5	1-MeO-2-iso-propylbenzene	1118	50.9±3.8 [Table S3]	51.6	-0.7
86-26-0	2-MeO-biphenyl	1511	57.8±0.5 [Table 1]	57.6	0.2
578-58-5	1-MeO-2-methylbenzene	1005	50.2±0.4 [13]	49.9	0.3
14804-32-1	1-MeO-2-ethylbenzene	1060	51.2±1.6 [16]	50.7	0.5

^a Kovats indices, J_x , on the standard non-polar columns from [18].

^b Calculated using equation $\Delta_f^g H_m^o(298.15 \text{ K}) = 34.6 + 0.0152 \times J_x$ with $R^2 = 0.9775$, with the assessed expanded uncertainty of $\pm 1.0 \text{ kJ}\cdot\text{mol}^{-1}$ (0.95 level of confidence, $k = 2$).

^c Difference between column 4 and 5 in this table.

Table S6

Correlation of vaporization enthalpies, $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K})$, of dialkyl ethers with their Kovats indices (J_{x})

CAS	Ether	J_{x}^{a}	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K})_{\text{exp}}^{\text{b}}$	$\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K})_{\text{calc}}^{\text{c}}$	Δ^{d}
		K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
598-53-8	methyl iso-propyl ether	462	26.8±0.2	26.2	0.6
6795-87-5	methyl sec-butyl ether	564	30.4±0.2	30.7	-0.3
627-02-1	ethyl iso-butyl ether	646	34.1±0.2	34.2	-0.1
2679-87-0	ethyl sec-butyl ether	648	34.2±0.2	34.2	0.0
627-08-7	n-propyl iso-propyl ether	650	34.0±0.2	34.5	-0.5
1860-27-1	n-butyl iso-propyl ether	725	38.8±0.2	38.7	0.1
15268-49-2	n-propyl iso-butyl ether	740	38.3±0.2	38.5	-0.2
61962-23-0	n-propyl sec-butyl ether	744	37.9±0.2	38.6	-0.7
628-55-7	di-iso-butyl ether	808	41.2±0.2 [20]	40.9	0.3
6863-58-7	di-sec-butyl ether	786	40.9±0.2	40.6	0.3
5756-37-6	n-pentyl iso-propyl ether	826	42.7±0.2	42.3	0.4
931-56-6	methoxy-cyclohexane	840		42.8±1.0	

^a Kovats indices, J_{x} , on the standard non-polar columns from [21].

^b Experimental values from [12].

^c Calculated using equation $\Delta_{\text{f}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K})/(\text{kJ}\cdot\text{mol}^{-1}) = 5.8 + 0.0441 \times J_{\text{x}}$ with ($R^2 = 0.9885$) with the assessed expanded uncertainty of $\pm 1.0\text{ kJ}\cdot\text{mol}^{-1}$ (0.95 level of confidence, $k = 2$).

^d Difference between column 4 and 5 in this table.

Table S7

Correlation of the normal boiling temperatures, T_{b} , of dialkyl ethers with their J_{x} (retention indices)

CAS	Ether	$T_{\text{b}}/\text{K}^{\text{a}}$	$J_{\text{x}}(\text{exp})^{\text{b}}$	$J_{\text{x}}(\text{calc})^{\text{c}}$	Δ^{d}
598-53-8	methyl iso-propyl ether	303.9		462	
6795-87-5	methyl sec-butyl ether	332.2		564	
627-02-1	ethyl iso-butyl ether	354.3	646	644	2
2679-87-0	ethyl sec-butyl ether	354.4	648	644	4
627-08-7	n-propyl iso-propyl ether	356.2		650	
1860-27-1	n-butyl iso-propyl ether	382.3	725	744	-19
15268-49-2	n-propyl iso-butyl ether	381.0		740	
61962-23-0	n-propyl sec-butyl ether	382.2		744	
628-55-7	di-iso-butyl ether	396.2	808	794	14
6863-58-7	di-sec-butyl ether	394.2	786	787	-1
5756-37-6	n-pentyl iso-propyl ether	405.2		826	
931-56-6	methoxy-cyclohexane	409.0 ^e		840	

^a Normal boiling temperatures are from Ref. [9–11].

^b Kovats indices, J_{x} , on the standard non-polar columns from [21].

^c Calculated using equation $J_{\text{x}} = -629.8 + 3.594 \times T_{\text{b}}$ with $R^2 = 0.974$

^d Difference between column 4 and 5 in this table.

^e From Table S3.

Table S8

Enthalpies of fusion ($\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}$), vaporization ($\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}$) and sublimation ($\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}$) of auxiliary compounds at melting points (T_{fus}) and 298 K (in $\text{kJ}\cdot\text{mol}^{-1}$)^a

Compound	T_{fus} K	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}})$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298\text{ K})^{\text{b}}$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298\text{ K})$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(298\text{ K})$ $\text{kJ}\cdot\text{mol}^{-1}$
4-iso-propyl-phenol [22]	334.1	14.5 ± 0.2	12.5 ± 0.6	82.8 ± 1.0	70.3 ± 1.2
4-sec-butyl-phenol [22]	335.2	17.3 ± 0.2	15.1 ± 0.7	89.1 ± 0.6	$74.0\pm0.9^{\text{c}}$
2-phenyl-phenol [23]	333.7	15.5 ± 0.2	13.3 ± 0.7	88.1 ± 1.2	$72.6\pm1.4^{\text{c}}$
3-phenyl-phenol [23]	351.0	$25.0\pm1.5^{\text{d}}$	21.8 ± 1.8	$106.8\pm2.1^{\text{e}}$	$85.0\pm1.0^{\text{e}}$
4-phenyl-phenol [23]	443.0	31.6 ± 0.2	22.7 ± 2.7	108.2 ± 1.2	$85.5\pm3.0^{\text{e}}$

^a Uncertainties are presented as expanded uncertainties (0.95 level of confidence with $k=2$).

^b The $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}$ at T_{fus} were adjusted to 298.15 K using Eq. (S9). Uncertainties were estimated with 30 % of the total adjustment [6,7].

^c Difference of columns 5 and 4 in this table.

^d Calculated using Eq. (S12) with the $\text{WC} = 71.3\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (see below Eq. 13).

^e Sum of columns 6 and 4 in this table. For comparison $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298\text{ K}) = 109.2\pm2.0\text{ kJ}\cdot\text{mol}^{-1}$ [24].

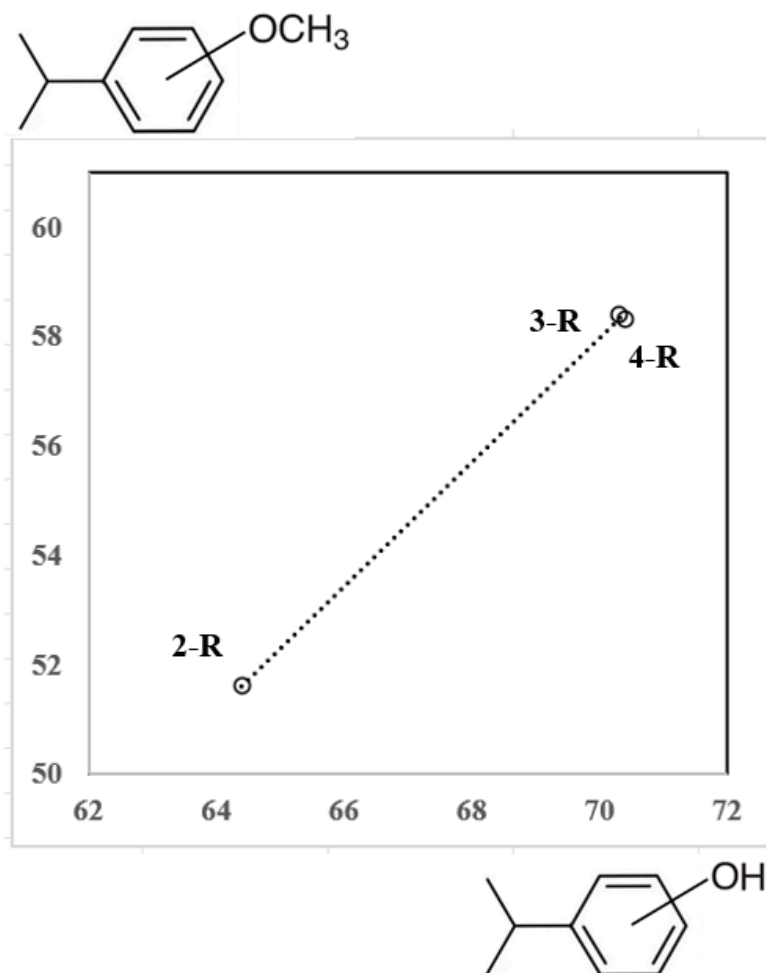


Figure S1. Correlation of vaporisation enthalpies, $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(298.15\text{ K})$, of hydroxy-iso-propylbenzenes and methoxy-iso-propylbenzenes. All values are in $\text{kJ}\cdot\text{mol}^{-1}$ with R = position of the substituent on the benzene ring.

Estimation of fusion enthalpies according to the Walden's Rule [25]

In 1908 Paul Walden found that the ratio according to Eq. (S12) can be considered as a constant (*Walden's Constant*) [26]:

$$WC = \frac{\Delta_{cr}^l H_m^o}{T_{fus}} = \Delta_{cr}^l S_m^o = 56.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad (\text{S12})$$

This observation was supported by experimental results from 35 compounds (mostly substituted benzenes like nitrobenzene, aniline, dimethylaniline, diphenylmethane, diphenylamine, acetophenone, *para*-propenylanisole, but also aliphatic esters, anhydrides, *etc.*). The prerequisite for this constancy is that the compounds did not associate in the liquid state. Eq. (S12) is known as Walden's rule for thermochemistry [27].

From a practical point of view and based on our experience, Eq. S12 can be easily adapted for calculations within a range of similarly shaped molecules. We have already observed similarity of *Walden's Constants* for R-acetanilides with R = alkyl, F, Cl, Br, NO₂, NH₂, OH, OCH₃ [17] and for the for R-substituted benzamides [28]. We have found that for these series the *WC* for each series deviates from the “classic” value 56.5 J·K⁻¹·mol⁻¹ by about ± 10 J·K⁻¹·mol⁻¹. Such a “modified” *Walden's Constant* helps not only in evaluating the consistency of the experimental fusion data within a set of similarly structured compounds, but also the *Walden's rule* serves as a valuable tool for estimating missing fusion enthalpies of interesting compounds, provided that their fusion temperatures are available. Moreover, the “modified” *Walden's Rule* often helps to evaluate available phase transition data. The WC for 4-phenyl-phenol was calculated according to Eq. (S12) as follows:

$$WC = \frac{\Delta_{cr}^l H_m^o}{T_{fus}} = \frac{22700}{443} = 71.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad (\text{S13})$$

This value was also adopted to be valid for 3-phenyl-phenol (see Table S10).

Table S9

Correlation of vaporization enthalpies, $\Delta_1^g H_m^o(298.15 \text{ K})$, of substituted phenols with their Kovats indices (J_x)

CAS	Compound	J_x^a	$\Delta_1^g H_m^o(298.15 \text{ K})_{\text{exp}}$	$\Delta_1^g H_m^o(298.15 \text{ K})_{\text{calc}}^b$	Δ^c
		K	kJ·mol ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹
99-71-8	4-sec-butyl-phenol	1318	74.0±0.5 [Table S8]	73.2	0.8
618-45-1	3-iso-propyl-phenol	1228		70.4	
99-89-8	4-iso-propyl-phenol	1247	70.3±0.5 [Table S8]	71.0	-0.7
580-51-8	3-phenyl-phenol	1704		85.0	

^a Kovats indices, J_x , on the standard non-polar columns from [21].

^b Calculated using equation $\Delta_1^g H_m^o(298.15 \text{ K}) = 32.7 + 0.0307 \times J_x$ with $R^2 = 0.9906$, with the assessed expanded uncertainty of ±1.0 kJ·mol⁻¹ (0.95 level of confidence, k = 2).

^c Difference between column 4 and 5 in this table.

Table S10Thermochemical data at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for reference compounds (in $\text{kJ}\cdot\text{mol}^{-1}$)

Compounds	$\Delta_f H_m^\circ(\text{liq})$	$\Delta_l^\circ H_m^\circ$	$\Delta_f H_m^\circ(\text{g})$
benzene [29]	49.0±0.9	33.9±0.1	82.9±0.9
methoxy-benzene [8]	-116.9±0.7	46.4±0.2	-70.3±0.7
biphenyl [14]	113.9±1.1	65.8±0.2	179.7±1.1
cyclohexane [30]	-156.4±0.8	33.1±0.2	-123.4±0.8
bicyclohexane [31]	-273.5±1.5	59.4±0.3	-214.1±1.5
methoxy-cyclohexane	-313.7±3.5	43.0±0.5 [Table 2]	-270.7±3.5 [Table 6]
iso-propyl-benzene [30]	-41.1±1.0	45.0±0.2	4.0±1.0
iso-propyl-cyclohexane		44.0±0.2 [32]	-196.2±3.5 ^a
2-hydroxy-iso-propylbenzene		64.4±0.4 [22]	-146.1±3.5 ^b
3-hydroxy-iso-propylbenzene		70.3±1.2 [22]	-149.9±3.5 ^b
4-hydroxy-iso-propylbenzene		68.9±3.0 [22]	-148.0±3.5 ^b
2-phenyl-phenol		72.6±1.4 [23]	
3-phenyl-phenol		87.4±3.0 [23]	
4-phenyl-phenol		85.5±3.0 [23]	
acetone [30]	-248.1±0.7	30.8±0.2	-217.3±0.7
iso-propanol [30]	-318.1±0.5	45.3±0.2	-272.8±0.5

^a Calculated with G4 method using the atomisation reaction.^b Calculated with G4 method using the WBR reaction (see Table 6).**Table S11**Correlation of the normal boiling temperatures, T_b , of dialkyl ethers with the standard molar enthalpies of vaporization, $\Delta_l^\circ H_m^\circ(298.15 \text{ K})$

CAS	Ether	T_b ^a	$\Delta_l^\circ H_m^\circ(298.15 \text{ K})_{\text{exp}}^b$	$\Delta_l^\circ H_m^\circ(298.15 \text{ K})_{\text{calc}}^c$	Δ^d
		K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
598-53-8	methyl iso-propyl ether	303.9	26.8±0.2	26.2	0.6
6795-87-5	methyl sec-butyl ether	332.2	30.4±0.2	30.7	-0.3
627-02-1	ethyl iso-butyl ether	354.3	34.1±0.2	34.2	-0.1
2679-87-0	ethyl sec-butyl ether	354.4	34.2±0.2	34.2	0.0
627-08-7	n-propyl iso-propyl ether	356.2	34.0±0.2	34.5	-0.5
1860-27-1	n-butyl iso-propyl ether	382.3	38.8±0.2	38.7	0.1
15268-49-2	n-propyl iso-butyl ether	381.0	38.3±0.2	38.5	-0.2
61962-23-0	n-propyl sec-butyl ether	382.2	37.9±0.2	38.6	-0.7
628-55-7	di-iso-butyl ether	396.2	41.2±0.2 [20]	40.9	0.3
6863-58-7	di-sec-butyl ether	394.2	40.9±0.2	40.6	0.3
5756-37-6	n-pentyl iso-propyl ether	405.2	42.7±0.2	42.3	0.4
931-56-6	methoxy-cyclohexane	409.0 ^e		42.9±0.6	
103754-94-5	1-methoxy-2-iso-propyl-cyclohexane	458.2		50.7±0.6	

^a Normal boiling temperatures are from Ref. [9–11].^b Experimental values from [12].^c Calculated using equation $\Delta_l^\circ H_m^\circ(298.15 \text{ K}) = -22.2 + 0.1592 \times T_b$ with $R^2 = 0.993$.with the assessed expanded uncertainty of $\pm 0.6 \text{ kJ}\cdot\text{mol}^{-1}$ (0.95 level of confidence, $k = 2$).^d Difference between column 4 and 5 in this table.^e From Table S3.^d Experimental value from Ref. [33].

Basics of the group-additivity concept ("centerpiece" approach)

Group additivity (GA) methods are successfully used to predict both the gas-phase enthalpies of formation and vaporisation enthalpies. The idea behind conventional GA methods is to split the experimental enthalpies of molecules into relatively small groups in order to obtain well-defined numerical contributions for them. The prediction then proceeds as construction of a framework of desired model molecule from the appropriate number and type of these contributions. Comprehensive systems of group contributions (or increments) are developed, covering the main classes of organic compound. Admittedly, the applicability of GA in the case of cyclic molecules is limited. To overcome this limitation, various ring corrections are implemented in the GA parameterization, however, each correction term is specific only to a particular unsubstituted ring (*e.g.* for cyclobutane, cyclopentane, cyclohexane, *etc.*). However, any type of substitution significantly affects ring strain due to intense interactions of the substituent(s) with the ring. The idea of the "centerpiece" approach is to select a potentially large "centerpiece" molecule that has a reliable enthalpy and that can generally mimic the structure of the molecule of interest. Then the necessary groups or blocks are attached to the "centerpiece", resulting in the construction of the desired molecule. A prerequisite for this method is that reliable experimental data are available for the selected "centerpiece" molecule.

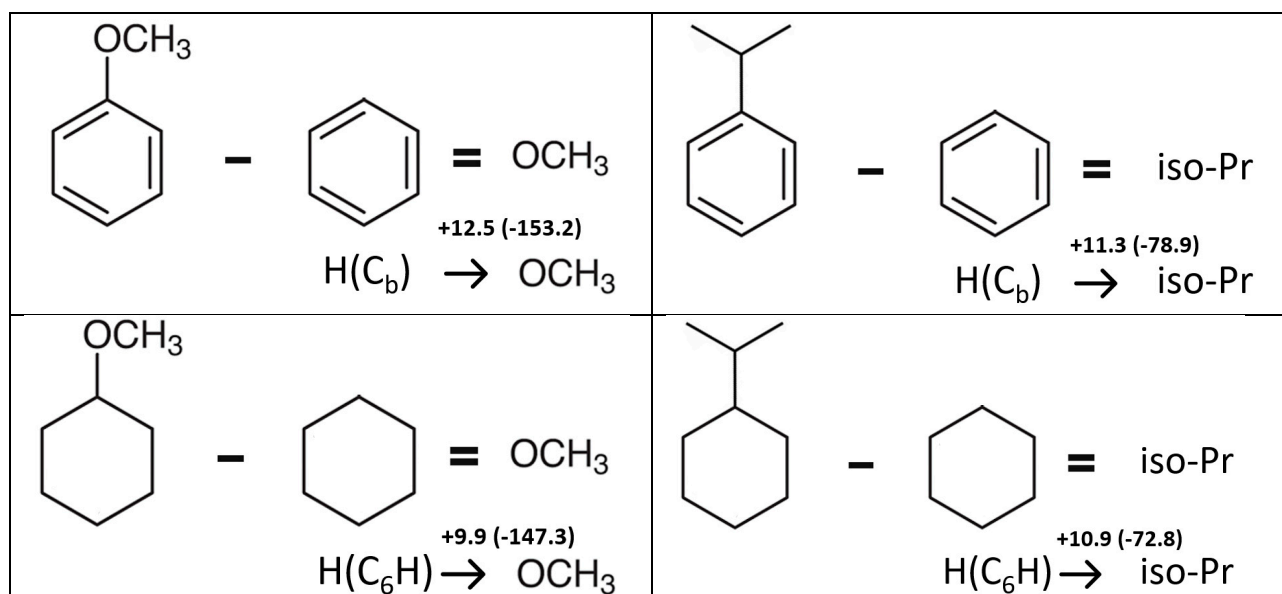


Figure S2 The development of the contributions for calculating the vaporization enthalpies (or gas-phase enthalpies of formation) of aromatic and cyclic aliphatic hydrocarbons using the "centerpiece" approach. All values in $\text{kJ}\cdot\text{mol}^{-1}$. The numerical values of the contributions for the enthalpy of formation are given in parentheses after the contributions for the enthalpy of vaporisation.

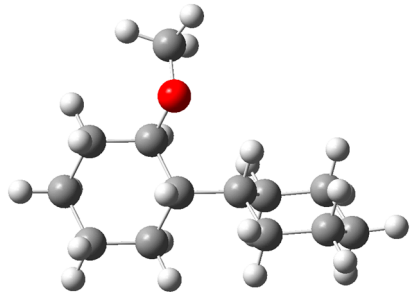
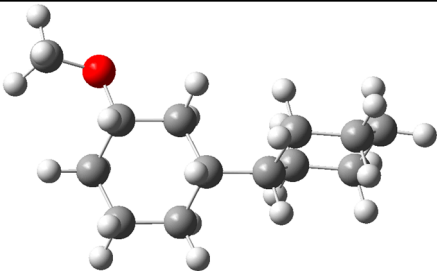
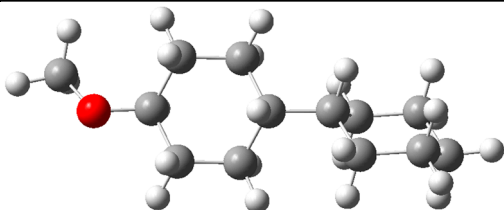
Table S12

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

	$\Delta_f^g H_m^o$	$\Delta_f H_m^o(g)$
	I_i [34] [35]	I_i [36]
Alkanes		
C-(C)(H) ₃	5.65	-42.05
C-(C) ₂ (H) ₂	4.98	-21.46
C-(C) ₃ (H)	3.01	-9.04
C-(C) ₄	0.01	-1.26
six-ring	1.88	5.40
Ethers		
O-(C) ₂	8.78	-99.23
C-(O)(H) ₃	5.65	-42.05
C-(O)(C)(H) ₂	4.60	-33.06
C-(O)(C) ₂ (H)	1.96	-25.64
C-(O)(C) ₃	-1.88	-18.16
Aromatics		
C _b -(C _b) ₂ (H)	5.65	13.82
C _b -(C _b) ₂ (C)	4.10	23.05
C _b -(C _b) ₂ (O)	3.72	1.88
C _b -(C _b) ₃ (biphenyl)	4.65	20.75

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 ($p^\circ = 0.1$ MPa) for methoxy-bicyclohexyls (in $\text{kJ} \cdot \text{mol}^{-1}$)

compound	structures	$\Delta_f H_m^o(g)_{G4}^a$
2-methoxy-bicyclohexyl		-367.5
3-methoxy-bicyclohexyl		-367.6
4-methoxy-bicyclohexyl		-366.9

1-methoxy-2-isopropyl-cyclohexane		-346.1
1-methoxy-3-isopropyl-cyclohexane		-346.8
1-methoxy-4-isopropyl-cyclohexane		-346.0

^a Calculated according to the G4 method using the atomization procedure.

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