

Supplementary Materials: Energetics of LOHC: Structure-Property Relationships from Network of Thermochemical Experiments and in Silico Methods

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Table S1. Provenance, purity, methods of purification and analysis of chemicals used in this work.

Compound	CAS	Source	Initial purity	Final purity ^a
2-methyl-quinoxaline	7251-61-8	TCI	98%	0.999
2,3-di-methyl-quinoxaline	2379-55-7	Alfa	97%	0.998

^a Purification was performed by the fractional distillation in vacuum for the liquids and fractional sublimation for solids. Mass fraction impurity was determined by the gas chromatography.

Transpiration Method: Vapor Pressure Measurements

Vapor pressures of pyrazine derivatives were measured using the transpiration method [1–3]. About 0.5 g of the sample was mixed with small glass beads and placed in the thermostatted U-shaped saturator. A nitrogen stream with well-defined flow rate was passed through the saturator at a constant temperature (± 0.1 K), and the transported material was collected in a cold trap. The amount of condensed sample was determined by GC analysis using the *n*-alkanes as an external standard. The absolute vapor pressure p_i at each temperature T_i was calculated from the amount of the product, collected within a definite period.

In our apparatus, the contribution due to diffusion was negligible at a flow rate up to $0.45 \text{ dm}^3 \cdot \text{h}^{-1}$. The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration was at a flow rate of $9.0 \text{ dm}^3 \cdot \text{h}^{-1}$. Thus, we carried out the experiments in the flow rate interval of $(2 \text{ to } 4) \text{ dm}^3 \cdot \text{h}^{-1}$, which has ensured that the transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The saturation vapor pressure p_{sat} at each temperature T_i was calculated from the amount of the material collected in the cold trap within a definite period of time. The amount of the transported material was determined by the GC analysis using an external standard (hydrocarbon $n\text{-C}_n\text{H}_{2n+2}$). Assuming validity of the Dalton's law applied to the nitrogen stream saturated with the substance *i*, values of p_i were calculated with equation:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i \quad (\text{S1})$$

$$V = V_{\text{N}_2} + V_i = (n_{\text{N}_2} + n_i) \cdot R \cdot T_a / P_a, \quad (\text{S2})$$

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 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-HAF-BLF0200C2AX5 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 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 calibrated digital flow rate sensor.

Table S2. Results of transpiration method for quinoxaline derivatives: absolute vapor pressures p , standard molar vaporization/sublimation enthalpies and standard molar vaporization/sublimation entropies.

$T/$ K ^a	$m/$ mg ^b	$V(N_2)^c /$ dm ³	$T_s/$ K ^d	$Flow/$ dm ³ ·h ⁻¹	$p/$ Pa ^e	$u(p)/$ Pa ^f	$\Delta_{l,cr}^g H_m^o(T)$ kJ mol ⁻¹	$\Delta_{l,cr}^g S_m^o(T)$ J·K ⁻¹ ·mol ⁻¹
2-methyl-quinoxaline: $\Delta_{l,cr}^g H_m^o(298.15 \text{ K}) = (64.04 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p/p^o) = \frac{300.6}{R} - \frac{85630.2}{RT} - \frac{70.7}{R} \ln \frac{T}{298.15}$								
288.7	0.71	5.692	295.9	3.08	2.14	0.06	65.22	136.5
293.5	0.68	3.539	295.9	3.08	3.31	0.09	64.88	135.3
298.4	0.59	2.000	295.9	3.08	5.08	0.15	64.53	134.0
303.4	0.49	1.077	295.9	3.08	7.75	0.22	64.18	132.9
308.3	0.63	0.897	295.9	3.08	12.04	0.33	63.84	132.1
313.2	1.08	1.035	295.9	4.14	17.86	0.47	63.49	130.9
318.1	0.75	0.513	295.9	3.08	25.07	0.65	63.14	129.5
323.1	1.65	0.769	295.9	3.08	36.57	0.94	62.79	128.5
328.0	1.54	0.513	295.9	3.08	51.30	1.31	62.44	127.4
332.0	2.04	0.513	295.9	3.08	67.86	1.72	62.16	126.6
2,3-di-methyl-quinoxaline: $\Delta_{l,cr}^g H_m^o(298.15 \text{ K}) = (84.6 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$								
$\ln(p/p^o) = \frac{306.5}{R} - \frac{94030.2}{RT} - \frac{31.5}{R} \ln \frac{T}{298.15}$								
313.2	5.35	45.900	293.2	4.34	1.79	0.05	84.16	177.9
318.3	5.68	29.275	293.2	4.34	2.99	0.08	84.00	177.3
323.3	3.55	11.710	293.2	4.34	4.67	0.12	83.85	176.5
328.3	5.36	10.987	293.2	4.34	7.52	0.21	83.69	176.0
333.2	8.32	10.409	293.2	4.34	12.3	0.3	83.53	175.9
338.1	14.68	11.638	293.2	4.34	19.4	0.5	83.38	175.5
343.2	9.15	4.988	293.2	4.34	28.3	0.7	83.22	174.5
348.0	6.59	2.385	293.2	4.34	42.6	1.1	83.07	174.1
348.1	5.49	1.954	293.2	2.06	43.2	1.1	83.07	174.2
353.0	7.59	1.807	293.2	4.34	64.7	1.6	82.91	173.8
353.0	8.40	1.952	293.2	4.34	66.3	1.7	82.91	174.0
358.0	7.55	1.157	293.2	4.34	100.5	2.5	82.75	173.8
358.1	5.37	0.836	293.2	2.95	98.8	2.5	82.75	173.6
363.0	5.53	0.607	293.2	2.14	140.2	3.5	82.59	172.9
368.0	6.90	0.514	293.2	2.06	206.3	5.2	82.44	172.6
372.5	9.62	0.514	293.2	2.06	287.3	7.2	82.30	172.3

^a Saturation temperature ($u(T) = 0.1 \text{ K}$). ^b Mass of transferred sample condensed at $T = 243 \text{ K}$. ^c Volume of nitrogen ($u(V) = 0.005 \text{ dm}^3$) used to transfer m ($u(m) = 0.0001 \text{ g}$) of the sample. ^d T_s is the temperature of the soap bubble meter used for measurement of the gas flow. ^e Vapour pressure at temperature T , calculated from the m and the residual vapour pressure at the condensation temperature calculated by an iteration procedure. ^f Uncertainties were calculated with $u(p_i/\text{Pa}) = 0.005 + 0.025(p_i/\text{Pa})$ for pressures below 5 Pa and with $u(p_i/\text{Pa}) = 0.025 + 0.025(p_i/\text{Pa})$ for pressures from 5 to 3000 Pa. The uncertainties for T , V , p , m , are standard uncertainties with 0.683 confidence level. Uncertainties of the vaporization/sublimation enthalpies are expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$). They were calculated according to a procedure described elsewhere [2,3]. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapor pressures, and uncertainties from adjustment of vaporization/sublimation enthalpies to the reference temperature $T = 298.15 \text{ K}$.

Vapor pressure data treatment

The temperature dependences of vapor pressure p measured in this work were fitted with the following equation [1]:

$$R \ln p_i = a + \frac{b}{T} + \Delta_{l,cr}^g C_{p,m}^o \ln \left(\frac{T}{T_0} \right), \quad (\text{S3})$$

where a and b are adjustable parameters and $\Delta_{l,cr}^g C_{p,m}^o$ is the difference of the molar heat capacities of the gas and the liquid (or crystalline) phases respectively. T_0 appearing in

Equation (S3) is an arbitrarily chosen reference temperature (which has been chosen to be $T_0 = 298.15$ K) and R is the molar gas constant. Values of $\Delta_{l,cr}^g C_{p,m}^o$ used for the data treatment of vapor pressures in Equation (S3), given in Table S3 were estimated according to empirical procedure [4] based on the heat capacity values $C_{p,m}^o$ (liq or cr) calculated by using the group additivity method [5].

Vapor temperature dependences have been used to derive the standard molar enthalpy of vaporization/sublimation of pyrazine derivatives at different temperatures, T , using the following equation:

$$\Delta_{l,cr}^g H_m^o(T) = -b + \Delta_{l,cr}^g C_{p,m}^o T \quad (S4)$$

Entropies of vaporization at temperatures T were also derived from the temperature dependence of vapor pressures using Equation (S5):

$$\Delta_{l,cr}^g S_m^o(T) = \Delta_{l,cr}^g H_m^o/T + R \ln(p/p^o) \quad (S6)$$

Experimental absolute vapor pressures, coefficients a and b of Equation (S3), as well as values of $\Delta_{l,cr}^g H_m^o(T)$ and $\Delta_{l,cr}^g S_m^o(T)$ are given in Table S2 (primary data) and the results together with $\Delta_{l,cr}^g H_m^o$ for pyrazine derivatives available in the literature are collected in Table 1 (main text). Procedure for calculation of the combined uncertainties of the vaporization/sublimation enthalpies includes uncertainties from the transpiration experimental conditions, uncertainties in vapor pressure, and uncertainties in the temperature adjustment to $T = 298.15$ K as described elsewhere [2,3].

Table S3. Compilation of data on molar heat capacities $C_{p,m}^o$ and differences $\Delta_{l,cr}^g C_{p,m}^o$ of pyrazine derivatives, in $J \cdot K^{-1} \cdot mol^{-1}$, 298.15 K.

compound	$C_{p,m}^o$ (liq) ^a	$-\Delta_{l,cr}^g C_{p,m}^o$ ^b	$C_{p,m}^o$ (cr) ^a	$-\Delta_{cr}^g C_{p,m}^o$ ^b
2-methyl-quinoxaline	231.2	70.7	-	-
2,3-di-methyl-quinoxaline	259.6	78.1	205.0	31.5

^a Calculated according to the procedure developed by Chickos *et al.* [5] ^b Calculated according to the procedure developed by Chickos and Acree [4].

Table S4. Compilation of enthalpies of vaporization/sublimation $\Delta_{l,cr}^g H_m^o$ for pyrazine derivatives derived from the data available in the literature.

Compound	Technique ^a	T-range	$\Delta_{l,cr}^g H_m^o$	$\Delta_{l,cr}^g H_m^o$	Ref.	
			(T_{av})	(298.15 K) ^b		
		K	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$		
pyrazine(cr)	T	-	-	57.5±0.4	[6]	
pyrazine(liq)	T	-	-	42.0±0.6	[6]	
methylpyrazine (liq)	S	400-500	36.0	44.7±2.0	[7]	
	F	287.6-391.6	42.4±0.8	44.3±1.0	[8]	
	CGC	298	-	43.7±3.8	[9]	
	S	263.7-362.9	43.3±0.4	43.8±0.4	[10]	
	S	291.4-345.2	43.5±0.4	44.5±0.6	[11]	
				44.0±0.3^c	average	
ethyl-pyrazine (liq)	DC	363	57.9±1.9	48.8±1.9	[12]	
	T	283.5-313.1	48.3±1.0	48.3±1.0	[11]	
				48.4±0.9^c	average	
n-propyl-pyrazine (liq)	T	282.7-313.2	51.9±0.8	51.9±1.0	[11]	
tert-butyl-pyrazine (liq)	T	282.7-313.2	50.5±0.2	50.5±0.4	[11]	
2,3-dimethylpyrazine(liq)	T	280.6-308.2	48.1±0.8	47.8±1.0	[11]	
2,5-dimethylpyrazine (liq)	F	302.5-411.3	44.5±0.8	47.6±1.0	[8]	
	DC	329	52.8±1.1	48.9±1.1	[13]	
	CGC	298	-	47.2±4.4	[9]	
	T	291.6-335.2	47.3±0.6	48.2±0.8	[11]	

				48.2±0.5 ^c	average
2,6-dimethylpyrazine (cr)	T	278.7-307.5	63.7±1.0	63.5±1.4	[11]
2,6-dimethylpyrazine (liq)				45.3±1.4	[11]
2,3-diethyl-pyrazine (liq)	DC	384	69.8±1.7	52.6±1.7	[12]
	CGC	298		54.8±1.5	[11]
				53.8±1.1 ^c	average
trimethylpyrazine (liq)	DC	376	66.5±1.6	53.9±1.6	[14]
	T	278.5-323.4	51.5±0.8	51.6±1.0	[11]
				52.2±0.8 ^c	average
tetramethylpyrazine (cr)	DC	377	109.3±4.0	(94.6±4.0)	[14]
	T	293.7-343.1	75.9±0.6	76.5±1.0	[11]
tetramethylpyrazine (liq)				57.6±1.3	[11]

^a Techniques: T = transpiration; S = static; E = ebulliometry; DC = drop calorimetry; F = flow method; CGC = correlation gas chromatography; K = Knudsen effusion method. In this table, uncertainties of the vaporization/sublimation enthalpies are expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$). They were calculated according to a procedure described elsewhere [1,2]. Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapor pressures, and uncertainties from adjustment of vaporization/sublimation enthalpies to the reference temperature $T = 298.15$ K. Value in brackets was not involved in calculation of the average value.^b Vapor pressures available in the literature were treated using Equations (S3) and (S4) with help of heat capacity differences from Table S3 to evaluate the enthalpy of vaporization at 298.15 K in the same way as our own results in Table S2.^c Weighted mean value (the uncertainty was taken as the weighing factor). Values highlighted in bold were recommended for thermochemical calculations.

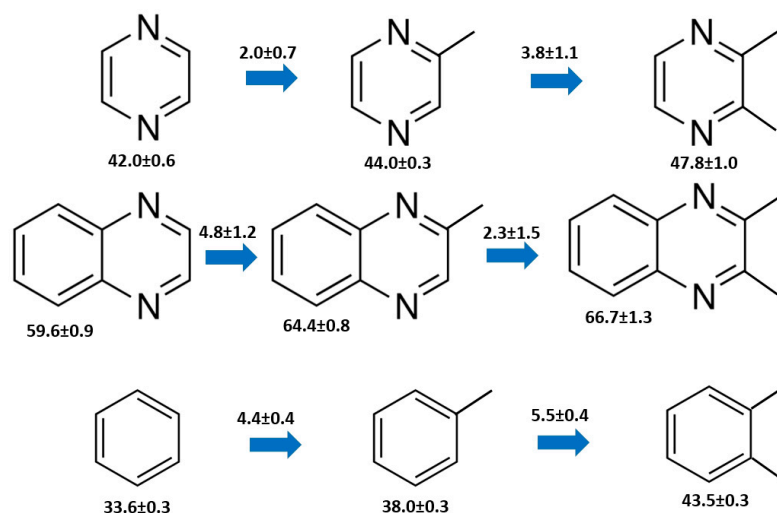


Figure S1. Comparison of vaporization enthalpies $\Delta_v^g H_m^o(298 \text{ K})$ of pyrazines (data are from Table S4), quinolones (data are from Table 1), and benzenes (data are from [20]). All data are in $\text{kJ}\cdot\text{mol}^{-1}$.

DSC: Enthalpy of fusion measurements. The thermal behavior of 2,3-dimethylquinoline including melting temperature and enthalpies of fusion was studied with a Mettler Toledo 822. Details are given elsewhere [15]. The instrument was standardized using indium metal with a mass fraction of 0.9999. The samples were hermetically sealed in 50 μL pans supplied by Perkin Elmer. The thermal behavior of the specimen was investigated during heating the sample with a rate of $10 \text{ K}\cdot\text{min}^{-1}$. The DSC measurements were repeated in triplicate and values agreed within the experimental uncertainties $u(\Delta_{\text{cr}}^{\text{L}} H_m^{\text{O}}) = 0.3 \text{ kJ}\cdot\text{mol}^{-1}$ for the enthalpy of fusion and $u(T) = 0.3 \text{ K}$ for the melting temperature. Uncertainties in the temperature adjustment of fusion enthalpies from T_{fus} to the reference temperature are estimates and amount to 30 % of the total adjustment [16].

The fusion enthalpies of pyrazine derivatives at T_{fus} K were measured by the (see Table 2). For the thermochemical calculations the experimental enthalpy of fusion has to be adjusted to the reference temperature $T = 298.15$ K. The adjustments were calculated with help of Equation (S6) [4]:

$$\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298.15 \text{ K})/(\text{J}\cdot\text{mol}^{-1}) = \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(T_{\text{fus}}/\text{K}) - (\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\circ} - \Delta_{\text{l}}^{\text{g}}C_{\text{p,m}}^{\circ}) \times [(T_{\text{fus}}/\text{K}) - 298.15 \text{ K}] \quad (\text{S6})$$

where $\Delta_{\text{cr}}^{\text{g}}C_{\text{p,m}}^{\circ}$ and $\Delta_{\text{l}}^{\text{g}}C_{\text{p,m}}^{\circ}$ were taken from Table S3. With this adjustment, the molar enthalpies of fusion, $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298.15 \text{ K})$ of pyrazine derivatives were calculated. The latter values were used for calculations of vaporization enthalpies according to the general equation:

$$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = \Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K}) - \Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\circ}(298.15 \text{ K}) \quad (\text{S7})$$

As well as for calculation of the liquid-phase enthalpies of formation according to the general Equation 8 (see main text). Results are given in Table S5.

Correlation of $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K})$ of pyrazine derivatives with Kovat's indices

The correlation of the enthalpies of vaporization with the Kovat's indices of the organic compounds is a valuable method to study the systematic behaviour in a homologous series. The vaporization enthalpy $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(298.15 \text{ K})$ also appears to be a function of the Kovats indices in different homologous series of alkanes, alcohols, aliphatic ethers, and alkylbenzenes [17–19]. In the Kovats retention index, J_x , used in gas chromatography, n -alkanes serve as the standards and logarithmic interpolation is utilized as defined by

$$J_x = \frac{\lg(t_x) - \lg(t_N)}{\lg(t_{N+1}) - \lg(t_N)} \times 100 + 100N \quad (\text{S8})$$

where x refers to the adjusted retention time t , N is the number of carbon atoms of the n -alkane eluting before, and $(N + 1)$ is the number of carbon atoms of the n -alkane eluting after the peak of interest. Thus, the retention time t_x of the compound of interest x is encompassed by retention times of the two n -alkanes.

Table S5. Thermochemical data at $T = 298.15 \text{ K}$ ($p^{\circ} = 0.1 \text{ MPa}$) for the pyridine and aniline derivatives, $\text{kJ}\cdot\text{mol}^{-1}$.

Compounds	$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{liq})_{\text{exp}}^{\text{a}}$	$\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}^{\text{a}}$	$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})_{\text{exp}}$	$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})_{\text{G4}}^{\text{b}}$
1	2	3	4	5
pyridine [20]	100.2±0.7	40.2±0.2	140.4±0.7	141.2
2-methyl-pyridine [20]	56.7±0.8	42.5±0.2	99.2±0.8	99.1
4-methylpyridine [20]	59.2±0.9	44.9±0.2	104.10.9	104.0
2,6-dimethylpyridine [20]	12.7±1.5	46.0±0.4	58.7±1.6	57.0
2-tert-butyl-pyridine ^c	-41.9±4.9	42.7±1.3	0.8±4.7	16.7
4-tert-butyl-pyridine [21]	-29.4±3.6	54.4±1.3	25.0±3.8	24.7
2,6-di-tert-butyl-pyridine [21]	-162.7±4.4	56.6±1.2	-105.5±4.6	-106.7
1,3,5-triazine [22]	184.7±0.9 ^d	41.2±0.5 ^d	225.9±1.0	226.1
aniline [20]	31.3±1.0	55.8±0.2	87.1±1.0	89.2
<i>N</i> -methyl-aniline [23]	35.9±2.1	55.0±0.2	90.9±2.1	94.8
<i>N,N</i> -dimethyl-aniline [24]	46.0±0.9	54.0±0.5	100.01.0	100.8
di-phenyl-amine [25]	146.7±2.0 ^d	79.0±0.8 ^d	225.7±2.2	-
tri-phenyl-amine	253.6±3.7 ^d	90.2±1.2 ^d	343.8±3.9	-

^a Experimental values taken from the literature. ^b Calculated by the atomization reaction. The theoretical $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})_{\text{G4}}$ values calculated by the atomisation procedure, were corrected using the linear correlation: $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})_{\text{exp}}/\text{kJ}\cdot\text{mol}^{-1} = (1.010 \pm 0.003) \Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{g})_{\text{G4}} + (0.7 \pm 0.4)$ with $R^2=0.9998$ developed in our previous work. [26]. ^c Calculated according to the Hess's Law applied to reaction: 2,6-di-tert-butyl-pyridine + benzene = 2-tert-butyl-pyridine + tert-butyl benzene. Data for tert-butyl-benzene were taken from [27]. ^d From Table 2 (recalculated from solid)

The G3MP2 method is less time-consuming in comparison to the G4. It has turned out, that the G4 calculations of the following molecules: 2,6-di-tert-butyl-pyrazine, 2,6-di-tert-butylpyridine, *N,N*-di-phenyl-amine and tri-phenyl-amine, performed on the Computational Centre of University of Rostock was not completed due to common time-restrictions. Thus, the computations have been conducted by the G3MP2 method. A linear

correlation between experimental and calculated by G3MP2 atomisation enthalpies of formation was established in our previous work [28]:

$$\Delta_f H_m^{\circ}(\text{g, exp})/\text{kJ}\cdot\text{mol}^{-1} = 0.992 \times \Delta_f H_m^{\circ}(\text{g, AT}) + 10.3 \quad (\text{S9})$$

Using this correlation the “corrected” enthalpies of formation of large molecules (2,6-*di-tert*-butylpyrazine, 2,6-*di-tert*-butylpyridine, *N,N*-*di*-phenyl-amine and *tri*-phenyl-amine) have been calculated (see Tables 8-9).

Table S6. Group-additivity values for calculation of enthalpies of vaporization, $\Delta_1^{\text{g}} H_m^{\circ}$ (298.15 K), of alkanes and amines at 298.15 K (in kJ mol⁻¹).

Increment	$\Delta_1^{\text{g}} H_m^{\circ}$
Alkanes	
C-(C)(H) ₃	6.33
C-(C) ₂ (H) ₂	4.52
C-(C) ₃ (H)	1.24
C-(C) ₄	-2.69
Amines^a	
C-(N)(C)(H) ₂	2.9
C-(N)(C) ₂ (H)	-2.0
C-(N)(C) ₃	-7.7
N-(C)(H) ₂	18.0
N-(C) ₂ (H)	12.6
N-(C) ₃	4.9
Ring-corrections	
aliphatic six-ring	5.9
piperidine six-ring	7.3
N-methyl-piperidine six-ring	7.3
piperazine six-ring	12.7
N-methyl-piperazine six-ring	10.6
N,N-dimethyl-piperazine six-ring	9.7
Nearest-neighbor-corrections	
C _t -C _q	1.9
1,2-di-methyl	-0.8
<i>ortho</i> -C _q -NH-C _s	3.7
2,6-C _q -NH-C _t	6.1

^a Validation of increments is given in Table S7.

Table S7. Experimental and estimated by group-additivity vaporization enthalpies at $T = 298.15$ K for cyclohexanamines (in kJ·mol⁻¹)^a.

compound	$\Delta_1^{\text{g}} H_m^{\circ}$ exp	$\Delta_1^{\text{g}} H_m^{\circ}$ add
cyclohexanamine	43.9±0.2	44.5
<i>N</i> -methyl-cyclohexanamine	46.4±0.3	44.9
<i>N,N</i> -dimethyl-cyclohexanamine	45.6±0.3	44.1
<i>N</i> -cyclohexyl-cyclohexanamine	64.1±0.3	65.1

^a Experimental data from [29].

Calculation of $\Delta_f H_m^{\circ}(\text{g})$ by using quantum-chemistry.

The latest G4 method from the G*-family is comparably more time consuming but it was found to be more accurate with a mean absolute deviation of 3.5 kJ·mol⁻¹ tested with 483 molecules of different structure and size in the G3/05 test set. Demonstration of agreement between two independent theoretical methods as well as with available experimental results can provide strong validation for both results and to establish thermochemical data of benchmark quality. Enthalpies H_{298} calculated by the G4 were converted to

enthalpies of formation $\Delta_f H_m^0(\text{g}, 298.15 \text{ K})$ using the conventional atomization reactions. Results of calculations are given in Tables S8–S11.










The $\Delta_f H_m^0(\text{g}, 298.15 \text{ K})$ -values required for thermodynamic analysis of hydrogenation/dehydrogenation reactions can be calculated according to the Hess's Law in two ways:

$$\Delta_r H_m^0(\text{g}) = \Delta_f H_m^0(\text{g}, \text{products}) - \Delta_f H_m^0(\text{g}, \text{reactants}) \quad (\text{S7})$$

$$\Delta_r H_m^0(\text{g}) = H_{298}(\text{g}, \text{products}) - H_{298}(\text{g}, \text{reactants}) \quad (\text{S8})$$






Both ways are not equivalent. As can be seen from Tables S8-S11 the $\Delta_r H_m^0(\text{g})$ -values calculated by Equation S10 are systematically of 5-10 $\text{kJ}\cdot\text{mol}^{-1}$ more negative in comparison to results by Equation S11. The possible reasons are usually explained for an imbalance of electronic energies calculated for the atomisation reaction participants. From our experiences, more elegant and reliable excess to the desired $\Delta_r H_m^0(\text{g}, 298.15 \text{ K})$ -values is calculation by Equation S11 directly from the H_{298} values calculated by a suitable QC method.

Table S8. Reaction enthalpy of hydrogenation/dehydrogenation of pyrazine derivatives, at $T = 298.15 \text{ K}$ ($p^\circ = 0.1 \text{ MPa}$) in $\text{kJ}\cdot\text{mol}^{-1}$.

Compounds ^a	$\Delta_f H_m^0(\text{g})_{\text{G4}^b}$	$\Delta_f H_m^0(\text{g})_{\text{G4}^c}$	$\Delta_r H_m^0(\text{g})_{\text{G4}^d}$	$\Delta_r H_m^0(\text{g})_{\text{G4}^e}$	
1	2	3	4	5	
pyrazine		209.9	32.0	-177.9	-168.7
methyl-pyrazine		162.7	-9.5	-172.2	-166.3
2,3-di-methyl-pyrazine		120.7	-42.9	-163.6	-157.8
2,5-di-methyl-pyrazine		119.7	-45.7	-165.4	-159.5
tri-methyl-pyrazine		77.3	-82.3	-159.6	-153.8
tetra-methyl-pyrazine		36.9	-118.2	-155.1	-149.4
tert-butyl-pyrazine		83.6	-82.1	-168.4	-159.8
2,6-di-tert-butyl-pyrazine		-29.9 ^f	-158.7 ^f	-129.9	-132.3
1,3,5-triazine		226.1	91.6	-134.5	-129.0








^a Only the fully dehydrogenated molecules are shown. ^b For the fully dehydrogenated molecules. ^c For the fully hydrogenated molecules. ^d Calculated as the difference between column 3 and 2 in this table. ^e Calculated from H_{298} -values of products and reactants of the hydrogenation reaction. ^f Calculated with the G3MP2 by using atomization (AT) procedure and corrected according to equation: $\Delta_f H_m^0(\text{g}, \text{exp})/\text{kJ}\cdot\text{mol}^{-1} = 0.992 \times \Delta_f H_m^0(\text{g}, \text{AT}) + 10.3$.

Table S9. Reaction enthalpy of hydrogenation/dehydrogenation of quinoxaline derivatives, at $T = 298.15 \text{ K}$ ($p^\circ = 0.1 \text{ MPa}$) in $\text{kJ}\cdot\text{mol}^{-1}$.

Compounds ^a	$\Delta_f H_m^0(\text{g})_{\text{G4}^b}$	$\Delta_f H_m^0(\text{g})_{\text{G4}^c}$	$\Delta_r H_m^0(\text{g})_{\text{G4}^d}$	$\Delta_r H_m^0(\text{g})_{\text{G4}^e}$	
quinoxaline		260.9	-43.8	-304.7	-294.7
2-methylquinoxaline		215.9	-83.7	-299.6	-289.7
2,3-di-methyl-quinoxaline		171.2	-118.9	-290.1	-280.3
2,6-di-methyl-1,5-naphthyridine		164.7	-125.7	-290.4	-280.6
phenazine		329.2	-120.1	-449.3	-435.1

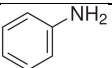
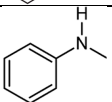
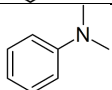
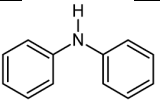
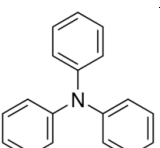
^a Only the fully dehydrogenated molecules are shown. ^b For the fully dehydrogenated molecules. ^c For the fully hydrogenated molecules. ^d Calculated as the difference between column 3 and 2 in this table. ^e Calculated from H_{298} -values of products and reactants of the hydrogenation reaction.

Table S10. Reaction enthalpy of hydrogenation/dehydrogenation of pyridine derivatives, at $T = 298.15$ K ($p^\circ = 0.1$ MPa) in $\text{kJ}\cdot\text{mol}^{-1}$.

Compounds ^a		$\Delta_f H_m^0(\text{g})_{\text{G4}^b}$	$\Delta_f H_m^0(\text{g})_{\text{G4}^c}$	$\Delta_r H_m^0(\text{g})_{\text{G4}^d}$	$\Delta_r H_m^0(\text{g})_{\text{G4}^e}$
pyridine		141.2	-43.3	-184.5	-178.6
2-methylpyridine		99.1	-81.7	-180.8	-174.7
4-methylpyridine		104.0	-77.1	-181.1	-175.1
2,6-dimethylpyridine		57.0	-119.8	-176.8	-170.9
2-tert-butylpyridine		16.7	-158.4	-175.1	-169.1
4-tert-butylpyridine		24.7	-151.2	-175.9	-170.0
2,6-di-tert-butylpyridine		-94.6 ^f	-258.9 ^f	-165.6	-168.1

^a Only the fully dehydrogenated molecules are shown. ^b For the fully dehydrogenated molecules. ^c For the fully hydrogenated molecules. ^d Calculated as the difference between column 3 and 2 in this table. ^e Calculated from H_{298} -values of products and reactants of the hydrogenation reaction. ^f Calculated with the G3MP2 by using atomization (AT) procedure and corrected according to equation: $\Delta_f H_m^0(\text{g, exp})/\text{kJ}\cdot\text{mol}^{-1} = 0.992 \times \Delta_f H_m^0(\text{g, AT}) + 10.3$.

Table S11. Reaction enthalpy of hydrogenation/dehydrogenation of aniline derivatives, at $T = 298.15$ K ($p^\circ = 0.1$ MPa) in $\text{kJ}\cdot\text{mol}^{-1}$.

Compounds ^a		$\Delta_f H_m^0(\text{g})_{\text{G4}^b}$	$\Delta_f H_m^0(\text{g})_{\text{G4}^c}$	$\Delta_r H_m^0(\text{g})_{\text{G4}^d}$	$\Delta_r H_m^0(\text{g})_{\text{G4}^e}$
aniline		89.2	-101.9	-191.1	-185.0
<i>N</i> -methylaniline		94.8	-94.2	-189.0	-183.0
<i>N,N</i> -dimethylaniline		100.8	-94.0	-194.8	-188.6
<i>N,N</i> -diphenylamine		214.7 ^f	-164.1 ^f	-381.8	-386.6
<i>tri</i> -phenyl-amine		320.0 ^f	-226.3 ^f	-550.7	-558.0

^a Only the fully dehydrogenated molecules are shown. ^b For the fully dehydrogenated molecules. ^c For the fully hydrogenated molecules. ^d Calculated as the difference between column 3 and 2 in this table. ^e Calculated from H_{298} -values of products and reactants of the hydrogenation reaction. ^f Calculated with the G3MP2 by using atomization (AT) procedure and corrected according to equation: $\Delta_f H_m^0(\text{g, exp})/\text{kJ}\cdot\text{mol}^{-1} = 0.992 \times \Delta_f H_m^0(\text{g, AT}) + 10.3$.

Table S12. Thermodynamic analysis of the dehydrogenation of ethylbenzene in the gas phase (at $p^\circ = 0.1$ MPa) calculated using G4 method and thermodynamic equilibrium constant K_p and K_a at 298 K and 400 K.

Reactants/Products	298.15 K (G4)		300 K (exp) ³⁰
	Free Energy	Enthalpy	
	Hartree		
ethylbenzene	-310.687825	-310.647334	
styrene	-309.477093	-309.4377	
hydrogen	-1.179507	-1.164715	
$\Delta_r G_m^0 / \text{kJ}\cdot\text{mol}^{-1}$	82.0		83.0
$\Delta_r H_m^0 / \text{kJ}\cdot\text{mol}^{-1}$	117.9		
$\Delta_r S_m^0 / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	120.6		
	$K_{p \text{ calc}} = 4.3 \times 10^{-15}$		$K_{p \text{ exp}} 3.5 \times 10^{-15}$
Reactants/Products	400 K (G4)		400 K (exp) ³⁰
	Free Energy	Enthalpy	
	Hartree		
ethylbenzene	-310.702532	-310.641574	
styrene	-309.491609	-309.432304	
hydrogen	-1.184735	-1.163587	
$\Delta_r G_m^0 / \text{kJ}\cdot\text{mol}^{-1}$	68.8		83.0
$\Delta_r H_m^0 / \text{kJ}\cdot\text{mol}^{-1}$	119.9		
$\Delta_r S_m^0 / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	128.0		
	$K_{p \text{ calc}} = 1.1 \times 10^{-9}$		$K_{p \text{ exp}} 3.3 \times 10^{-9}$

Table S13. Thermodynamic analysis of the hydrogenation of 2,5-di-methyl-pyrazine in the gas phase (at $p^\circ = 0.1$ MPa) calculated using G4 method and thermodynamic equilibrium constant K_p at 298 K and 400 K.

Reactants/Products	298 K		400 K	
	Free Energy	Enthalpy	Free Energy	Enthalpy
	Hartree			
2,5-dimethylpyrazine	-342.784133	-342.799215	-342.736913	-342.742438
$3 \times \text{H}_2$	3×-1.179507	-1.184735	-1.163587	-1.164715
2,5-dimethylpiperazine	-346.339086	-346.354357	-346.29063	-346.297345
$\Delta_r G_m^0 / \text{kJ}\cdot\text{mol}^{-1}$	-43.1		-2.5	
$\Delta_r H_m^0 / \text{kJ}\cdot\text{mol}^{-1}$	-159.5		-165.3	
$\Delta_r S_m^0 / \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	-390.4		-407.1	
$K_{p \text{ calc}}$	3.6×10^7		2.1	

Table S14. Experimental vapor pressures of hydrogenation/dehydrogenation reactions participants used for adjustment of the theoretical thermodynamic equilibrium constant K_p to the liquid phase equilibrium constant K_a .

Compounds	p , atm	p , atm	Ref.
	298 K	400 K	
pyrazine	0.0240	1.36	[6]
piperazine	0.0041	0.513	[31]
2,5-dimethylpyrazine	0.0036	0.388	[11]
2,5-dimethylpiperazine	0.0016	0.331	[32]

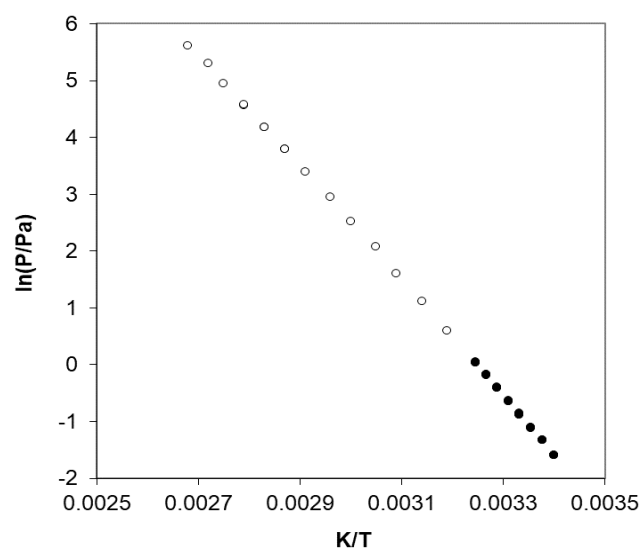


Figure S2. Temperature dependence of vapor pressures over the 2,3-di-methyl-quinoxaline: ○: this work; ●: [33]

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