

SUPPLEMENTARY MATERIAL

Enthalpies of Vaporization and Sublimation of the Halogen-Substituted Aromatic Hydrocarbons at 298.15 K: Application of Solution Calorimetry Approach

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Table S1. Experimental Enthalpies of Solution ($\Delta_{\text{soln}}H^{\text{A}_i/\text{S}}$) at Infinite Dilution of Halogen-Substituted Aromatic Hydrocarbons in Benzene Measured in This Work at 298.15 K and 0.1 MPa

solute (A_i)	solvent (S)	m/mg ^a	b/mol·kg ⁻¹ × × 10 ³ ^b	$\Delta_{\text{soln}}H^{\text{A}_i/\text{S}} /$ kJ·mol ⁻¹ ^c
1-bromo-4-chlorobenzene (cr)	benzene	74.6 70.5 97.7 98.5 88.9 86.7	3.4 3.2 7.9 7.7 11.9 11.7	17.42 17.60 17.67 17.80 17.70 17.80
				$\Delta_{\text{soln}}H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 17.67 \pm 0.15$
1,2-dibromobenzene (l)	benzene	26.0 26.0 26.0 26.0	1.0 1.9 2.9 3.9	1.16 1.15 1.16 1.16
				$\Delta_{\text{soln}}H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 1.16 \pm 0.01$
1,3-dibromobenzene (l)	benzene	25.7	1.0	1.97

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		25.7	1.9	1.84
		25.7	2.9	2.03
		25.7	3.8	2.12
$\Delta_{\text{soln}} H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 2.0 \pm 0.2$				
1,4-dibromobenzene (cr)	benzene	36.6	1.4	19.56
		40.1	1.5	20.12
		48.7	3.2	19.91
		46.4	3.2	19.65
$\Delta_{\text{soln}} H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 19.8 \pm 0.4$				
1-bromonaphthalene (l)	benzene	29.6	1.2	1.24
		29.6	2.5	1.24
		29.6	3.7	1.24
		29.6	5.0	1.25
$\Delta_{\text{soln}} H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 1.24 \pm 0.01$				
1-iodonaphthalene (l)	benzene	34.6	1.2	1.61
		34.6	2.4	1.80
		34.6	3.6	1.79
		34.6	4.8	1.61
$\Delta_{\text{soln}} H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 1.7 \pm 0.2$				
1,4-dibromonaphthalene (cr)	benzene	28.2	0.9	20.00
		35.9	1.1	20.41
		42.3	2.2	21.05
		40.6	2.3	21.00
		36.2	3.3	20.62
		32.0	3.3	20.54
$\Delta_{\text{soln}} H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 20.6 \pm 0.4$				
4-bromobiphenyl (cr)	benzene	56.6	2.1	19.97
		54.8	2.4	20.28
		49.5	4.0	19.90
		50.6	4.0	20.20
$\Delta_{\text{soln}} H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 20.1 \pm 0.3$				
4,4'-dibromobiphenyl (cr)	benzene	60.8	1.7	22.8
		62.1	1.7	23.3
		66.8	3.6	23.4
		63.5	3.5	22.7
$\Delta_{\text{soln}} H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 23.1 \pm 0.6$				
9-chloroanthracene (cr)	benzene	24.7	1.0	21.45
		25.9	1.1	21.19
		27.7	2.2	21.64
		24.4	2.1	21.46
		34.8	3.6	21.60
$\Delta_{\text{soln}} H^{\text{A}_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 21.5 \pm 0.2$				

9-bromoanthracene (cr)	benzene	20.8	0.7	21.20
		24.4	0.8	21.69
		19.2	1.4	21.41
		34.1	2.0	21.47
		35.6	2.6	21.24
		22.8	2.8	21.44
$\Delta_{\text{soln}} H^{\Delta_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 21.4 \pm 0.2$				
9,10-dichloroanthracene (cr)	benzene	20.3	0.7	27.55
		19.8	0.7	28.18
		19.6	1.4	27.00
		21.3	1.5	28.01
$\Delta_{\text{soln}} H^{\Delta_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 27.7 \pm 0.8$				
9,10-dibromoanthracene (cr)	benzene	14.2	0.4	24.20
		12.8	0.3	24.90
		10.8	0.6	25.18
		12.1	0.6	24.23
		15.3	1.0	25.30
$\Delta_{\text{soln}} H^{\Delta_i/\text{S}} / \text{kJ} \cdot \text{mol}^{-1} = 24.8 \pm 0.8$				

^a Mass of solute sample which was added in each dissolution experiment. ^b Molality of solute in benzene solution after experiments. ^c Enthalpy of solution of each experiment. Uncertainties in this table correspond to expanded uncertainties of the mean (0.95 level of confidence).

Table S2. Molar Refractions (MR^{A_i}) of Liquid Halogen-Substituted Aromatic Hydrocarbons, Calculated from Literature Values of Densities (d) and Refractive Indices (n) at Different Temperatures and 0.1MPa.

compound (A_i)	$Mr/g\cdot mol^{-1}$ ^a	T/K	$d/g\cdot cm^{-3}$	n	$MR^{A_i} /cm^3\cdot mol^{-1}$
1,3-dichlorobenzene	147.00	298.15	1.28276 ¹	1.5438 ¹	36.2
	147.00	293.15	1.2884 ²	1.5459 ²	36.1
	147.00	288.15	1.29408 ³	1.54965 ⁴	36.2
1,2-dibromobenzene	235.91	298.15	1.9759 ²	1.6086 ²	41.4
1,3-dibromobenzene	235.91	293.15	1.9250 ⁵	1.6078 ⁵	42.4
1-bromonaphthalene	207.07	293.15	1.4835 ⁶	1.6580 ⁶	51.4
	207.07	313.15	1.4648 ⁶	1.649 ⁷	51.5
1-iodonaphthalene	254.07	293.15	1.7396 ⁶	1.7028 ⁶	56.6

^a Molar mass of studied compounds

Table S3. Molar Refractions (MR^{A_i}) of Halogen-Substituted Aromatic Hydrocarbons Determined in This Work by Eqs (3)-(5) from Mole Fractions (x_i) and Experimentally Measured Densities (d) and Refractive Indices (n) of Their Solutions in Benzene at 298.15 K and 0.1MPa.

compound (A_i)	$x_i^a \cdot 10^4$	$d_{12}/\text{g}\cdot\text{cm}^{-3}$	n_{12}	$MR^{A_i} / \text{cm}^3 \cdot \text{mol}^{-1}$
1,2-dibromobenzene (l)	27.8 36.5 73.8 125.1	0.877563 0.878834 0.884292 0.891807	1.49816 1.49829 1.49882 1.49961	41.5 41.6 41.5 41.6
				d_S (benzene I) = 0.873478 n_S (benzene I) = 1.49776 $MR^{A_i} = 41.6 \pm 0.1$
1,4-dibromobenzene (cr)	18.0 18.5 25.0 33.0	0.876211 0.876342 0.877295 0.878419	1.49781 1.49784 1.49795 1.49808	43.1 42.7 42.8 43.0
				d_S (benzene II) = 0.873671 n_S (benzene II) = 1.49755 $MR^{A_i} = 42.9 \pm 0.3$
1-bromo-4-chlorobenzene (cr)	23.1 26.8 25.3	0.875875 0.876250 0.876093	1.49779 1.49782 1.49781	39.4 39.2 39.3
				d_S (benzene II) = 0.873613 n_S (benzene I) = 1.49755 $MR^{A_i} = 39.3 \pm 0.2$
hexachlorobenzene ^c (cr)	2.8 5.2 6.6 9.4	1.584372 1.584534 1.584525 1.584626	1.45724 1.45734 1.45735 1.45743	58.0 58.2 58.0 57.8
				d_S (carbon tetrachloride) = 1.584255 n_S (carbon tetrachloride) = 1.45715 $MR^{A_i} = 58.0 \pm 0.3$
1,4-dibromonaphthalene (cr)	8.7 20.8 18.9 32.1	0.875112 0.877158 0.876792 0.879019	1.49786 1.49828 1.49820 1.49872	61.6 60.9 61.3 62.0
				d_S (benzene II) = 0.873652 n_S (benzene II) = 1.49755 $MR^{A_i} = 61.5 \pm 0.7$
4-bromobiphenyl (cr)	10.9 18.6 18.9 23.7	0.874692 0.875469 0.875450 0.875983	1.49787 1.49810 1.49809 1.49820	61.5 61.5 61.8 60.4
				d_S (benzene II) = 0.873616 n_S (benzene II) = 1.49755 $MR^{A_i} = 61.3 \pm 1.0$
4,4'-dibromobiphenyl (cr)	11.6	0.875632	1.49802	71.1

10.7	0.875480	1.49796	70.0
9.0	0.875213	1.49791	69.7
7.6	0.875001	1.49787	69.3
d_S (benzene II) = 0.873633			
n_S (benzene II) = 1.49755			
$MR^A = 70.1 \pm 1.1$			

^a Mole fraction of studied compound in solution. ^b For measurements benzene from two different producers was used (benzene I – first producer, benzene II – second producer). ^c Carbon tetrachloride was used as a solvent due to low solubility of hexachlorobenzene in benzene. Standard uncertainties u are $u(x_i) = 5 \cdot 10^{-5}$, and the combined expanded uncertainties Uc are $Uc(d) = 3 \cdot 10^{-5} \text{ g} \cdot \text{cm}^{-3}$, $Uc(n) = 1 \cdot 10^{-4}$ (0.95 level of confidence).

DSC Measurements of Fusion Enthalpies of Halogen-Substituted Aromatic Hydrocarbons

Table S4 presents the experimental results on fusion enthalpies of halogen-substituted aromatic hydrocarbons at the temperature of measurements and reference temperature 298.15 K. For every compound several cycles “heating-cooling” from room temperature to 40 K higher than melting point were carried out. These experiments were reproduced several times. Obtained enthalpies of fusion were adjusted to the reference temperature 298.15 K using group-contribution approach proposed by Acree and Chickos.⁸ In order to verify obtained enthalpies of fusion thermostability of halogen-substituted aromatic hydrocarbons was analyzed using thermogravimetry method with simultaneous mass-spectrometric (MS) detection of the evolved vapors. Experiments were performed in the argon dynamic atmosphere ($75 \text{ ml}\cdot\text{min}^{-1}$) with the heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. 1,4-Dibromonaphthalene, 4-bromobiphenyl, 9-chloroanthracene, and 9,10-dibromoanthracene were stable up to temperature on 40 K higher than melting point. For example, DSC and TGA curves of 9-chloroanthracene are presented on Fig. S1. It is evident that practically there is no any mass loss in the studied temperature range. The same results were obtained for other compounds. The exception was only 9,10-dichloroanthracene. We have observed mass loss of 4.04 % near the melting point (see Fig. S2). Therefore, for 9,10-dichloroanthracene the additional analysis using modulated temperature scanning calorimetry⁹ was carried out. From the experimental data we determined the share of reversible (fusion) and irreversible (mass loss) processes 81.28% and 18.72%, respectively. Mass change was taken into account and the enthalpy of fusion of 9,10-dichloroanthracene was corrected.

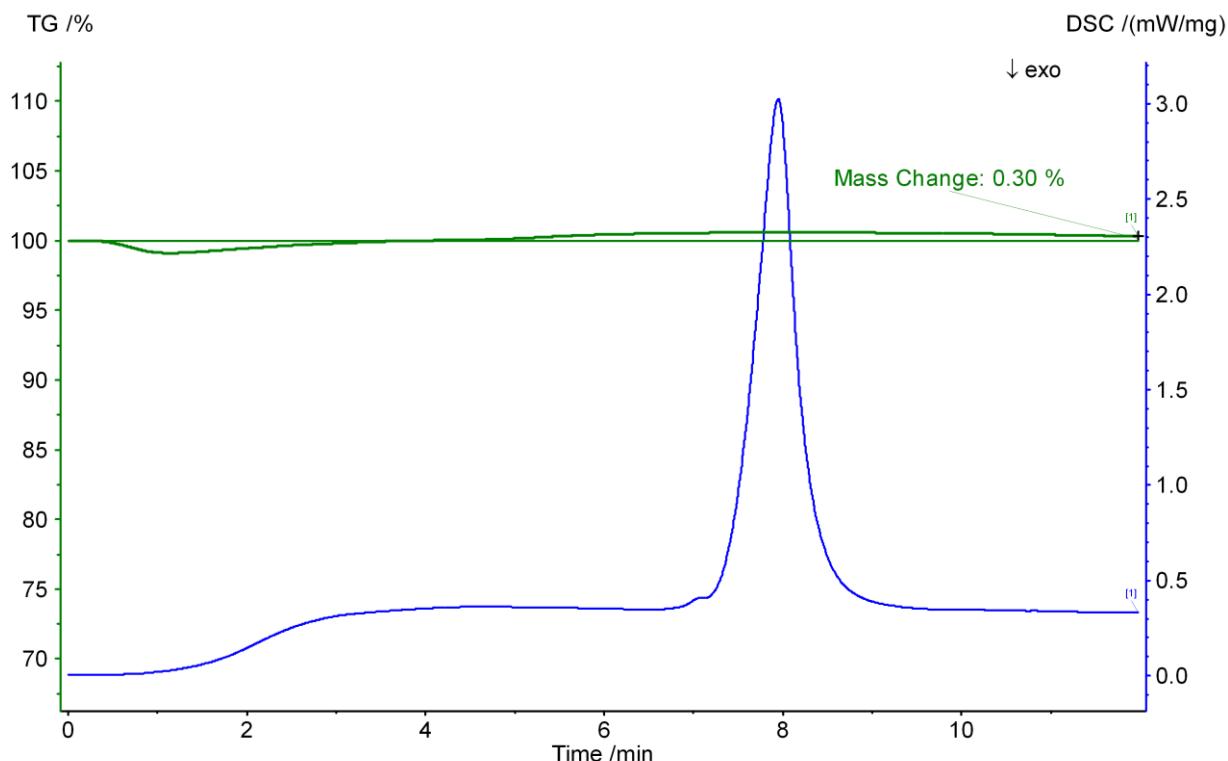


Figure S1. DSC (blue color) and TGA (green) curves of 9-chloroanthracene.

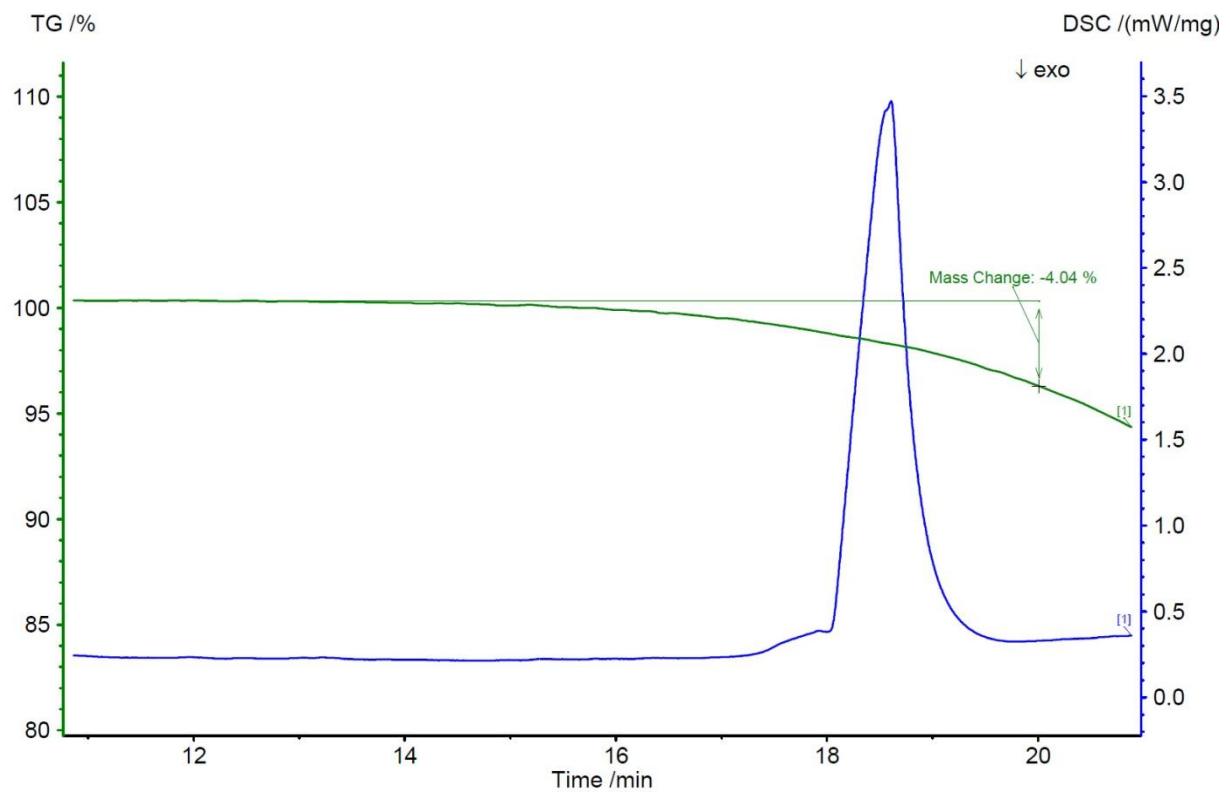


Figure S2. DSC (blue color) and TGA (green) curves of 9,10-dichloroanthracene.

Table S4. Enthalpies of Fusion of Several Halogen-Substituted Aromatic Hydrocarbons Measured in This Work

compound	$m \cdot 10^3$ g	$C_p^l (C_p^{cr})$ $J \cdot mol^{-1} \cdot K^{-1}$	T_m K	$\Delta_{cr}^l H_m (T_m)$ kJ · mol ⁻¹	$\Delta_{cr}^l H_m (298.15)$ kJ · mol ⁻¹
1,4-dibromonaphthalene (cr)	4.18	261.2 (203.8)	354.2	21.2	18.6
	4.18		352.7	20.7	18.1
	4.18		352.7	20.7	18.1
	4.78		353.6	21.5	18.8
	4.78		352.6	21.1	18.5
	4.78		352.6	21.1	18.5
					18.5±0.3
4-bromobiphenyl (cr) ^a	0.62	276.7 (215.4)	(337.1) 362.2	(4.2+16.3)	17.3
	0.63		(337.1) 362.0	(4.3+16.5)	17.6
	1.63		(337.1) 362.2	(4.3+16.1)	17.0
					17.3±0.5
9-chloroanthracene (cr)	5.54	303.5 (228.7)	379.4	22.0	17.5
	5.54		376.4	21.8	17.5
	5.54		376.8	21.7	17.4
	6.18		379.8	21.9	17.5
	6.18		374.5	22.1	18.0
	6.18		374.8	22.2	18.1
	6.18		374.2	22.2	18.0
					17.7±0.3
9,10-dichloroanthracene (cr)	4.83	327.8 (248.4)	486.6	25.3 ^b	14.4
	5.97		486.5	25.3 ^b	14.5
	4.00		486.6	24.6 ^b	13.7
					14.2±1.1

9,10-dibromoanthracene (cr)	4.85	335.4 (255.8)	498.1	28.2	16.5
	2.94		498.1	29.5	17.8
	2.94		497.4	29.1	17.5
	3.59		498.1	28.6	16.9
	3.59		497.6	28.2	16.5
	3.59		497.6	28.3	16.6
	3.99		498.1	29.0	17.2
	3.99		497.4	28.3	16.6
					17.0±0.4

^a Phase transition before melting was observed (at temperature given in brackets) and the sum of total solid state phase transitions for 4-bromobiphenyl was calculated as the sum of two peaks in column 5 and adjusted to the reference temperature.

^b Corrected values by modulated temperature and mass loss.

Uncertainties of Vapor Pressure Measurements. The experimental quantities measured to obtain the vapor pressures and enthalpies of vaporization are as follows:

(a) The mass, m_i , of compound collected in the cold trap. This amount was determined by GC analysis using an external standard. This GC procedure consists of two steps: calibration of the FID using two reference solutions and injecting of the mixture of the transported sample with the well-defined amount of the standard solution. For the first step, about 0.03 g of sample was weighed in 5 ml calibrated pycnometer, and about 0.05 g of the standard compound (hydrocarbon $n\text{-C}_n\text{H}_{2n+2}$) was weighed in 10 ml calibrated pycnometer. We used KERN ACJ 220-4m balances with the resolution of ± 0.0001 g. Both pycnometers were filled with acetonitrile with uncertainty ± 0.01 ml. Mixtures for the FID calibration were prepared using the Hamilton syringes of the Gastight 1700 series with 100 μl and 250 μl volume. Calibration mixtures were analyzed by GC with the repeatability within 1 to 2 %. For the mass determination the cold trap was charged with 200 μl of the standard solution from the 10 ml pycnometer using the syringe of 250 μl nominal volume and the mixture was analyzed by GC with the same reproducibility.

(b) The volume of the carrier gas $V_{\text{N}2}$. For the transpiration experiments with duration over few hours the value of $V_{\text{N}2}$ was directly measured by Honeywell S&C - HAFBLF0200C2AX5 digital flow rate sensor with uncertainty at the level of 2.5 %. For the shorter experiments the carrier gas flow rate was measured with the HP Agilent soap film flow meter (model 0101-0113). The value of $V_{\text{N}2}$ was calculated from the gas-flow and time measurements with uncertainty of 1 %.

(c) The temperature of saturator was kept constant within (± 0.2 K) using a circulating thermostat. The accurate measurement of temperature is done by using a calibrated Pt-100 thermometer with resolution of 0.2 K.

(d) The ambient temperature T_a of the volume $V_{\text{N}2}$ measurements was measured using the calibrated Pt-100 with uncertainty ± 0.2 K.

(e) The atmospheric pressure was measured using a digital pressure indicator with uncertainty ± 2 hPa absolute.

Uncertainties resulting from correlations are reported as standard deviations (u).

Uncertainties associated with combined results were evaluated as follows:

$$u(P)/P =$$

$(0.0001/0.05) = 0.0040 \times 100 = 0.20\%$	mass of the reference sample
$(0.0001/0.03) = 0.0067 \times 100 = 0.67\%$	mass of the sample under study
$(0.01/5) + (0.01/10) = 0.0030 \times 100 = 0.30\%$	volumes of calibrated pycnometers
$(0.25/200) + (0.1/100) = 0.0022 \times 100 = 0.22\%$	volumes of the standard solution

$(0.02/2) + (0.02/2) = 0.02 \times 100 = 2.0 \%$	GC injections (calibration + determination)
$(0.01/2) = 0.005 \times 100 = 0.5 \%$	volume of transporting gas
$(0.2/323) + (0.2/298) = 0.00129 \times 100 = 0.13 \%$	T -measurements (saturator + ambient)
$(2/1000) = 0.002 \times 100 = 0.20 \%$	ambient atmospheric pressure
$u(P)/P = (u_1^2 + u_2^2 + \dots)^{0.5} \times 100 = 2.1 \%$	<i>combined uncertainties</i>

It has turned out that accuracy of vapor pressures measured by transpiration method governed mostly by the reproducibility of the GC analysis as well as by the volume V_{N2} determination.

The standard uncertainties (u) of the measured vapor pressures have been calculated to be:

$$u(p/\text{Pa}) = 0.025 + 0.025(p/\text{Pa}) \text{ for } p > 5 \text{ to } 1000 \text{ Pa}$$

$$u(p/\text{Pa}) = 0.005 + 0.025(p/\text{Pa}) \text{ for } p < 5 \text{ Pa}$$

To validate system operation, the vapor pressure of naphthalene was determined at $p = (1$ to 500 Pa. Experimental vapor pressure of naphthalene obtained using this procedure agreed with the results reported in the literature¹⁰ to within (0.6 to 2.5) %. For validation of our uncertainty estimations we measured vapor pressures for series of *n*-alkanols¹¹ where reliable data at $p = (0.1$ to 1000) Pa from different methods were available. It has turned out that vapor pressures of *n*-alkanols derived from the transpiration method were comparable with available high-precision data generally within (1 to 3) % in agreement with our estimations.

Table S5. Parameters for the Calculation of Enthalpies of Vaporization of Dihalogen-Substituted Benzenes at 298.15 K (in $\text{kJ}\cdot\text{mol}^{-1}$) from ref. 12 ^a

Parameters	$\Delta_1^g H_m$ (298.15) $\text{kJ}\cdot\text{mol}^{-1}$	Parameters	$\Delta_1^g H_m$ (298.15) $\text{kJ}\cdot\text{mol}^{-1}$
benzene	33.9	<i>para</i> F-(<i>F</i> or <i>Cl</i>)	0.4
$\Delta H(H\rightarrow F)$	0.8	<i>para</i> F-(<i>Br</i> or <i>I</i>)	-0.5
$\Delta H(H\rightarrow Cl)$	7.9	(<i>Cl</i> - <i>Cl</i>)	-1.5
$\Delta H(H\rightarrow Br)$	10.4	(<i>Cl</i> - <i>Br</i>)	-0.7
$\Delta H(H\rightarrow I)$	14.9	(<i>Cl</i> - <i>I</i>)	0.0
<i>ortho</i> F-(<i>F</i> , <i>Cl</i> , <i>Br</i> , <i>I</i>)	1.5	(<i>Br</i> - <i>Br</i>)	0.0
<i>meta</i> F-(<i>F</i> or <i>Cl</i>)	0.0	(<i>Br</i> - <i>I</i>)	1.0
<i>meta</i> F-(<i>Br</i> or <i>I</i>)	-1.0	(<i>I</i> - <i>I</i>)	2.5

^a These parameters can be also applied in combination with the experimental vaporization enthalpies, $\Delta_1^g H_m$ (298.15 K), of naphthalene (55.4 ± 1.4) $\text{kJ}\cdot\text{mol}^{-1}$, biphenyl (64.9 ± 1.3) $\text{kJ}\cdot\text{mol}^{-1}$, and anthracene (80.6 ± 0.8) $\text{kJ}\cdot\text{mol}^{-1}$ used as the basic unities instead benzene.

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