Thermochemistry of Dihalogen-Substituted Benzenes: Data Evaluation Using Experimental and Quantum Chemical Methods

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S *Supporting Information*
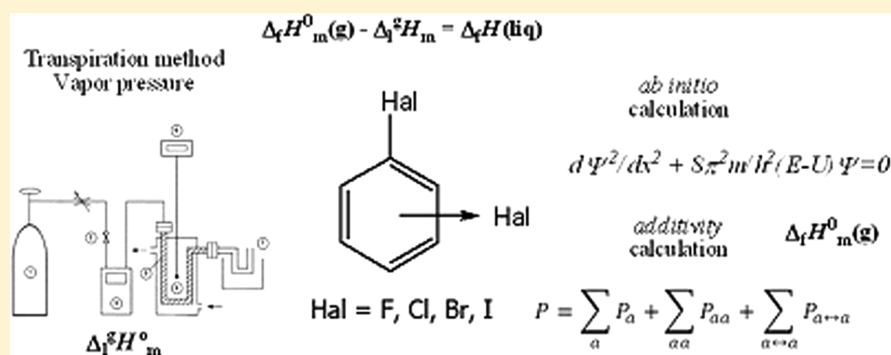
ABSTRACT: Temperature dependence of vapor pressures for 12 dihalogen-substituted benzenes (halogen = F, Cl, Br, I) was studied by the transpiration method, and molar vaporization or sublimation enthalpies were derived. These data together with results available in the literature were collected and checked for internal consistency using structure−property correlations. Gas-phase enthalpies of formation of dihalogen-substituted benzenes were calculated by using quantum-chemical methods. Evaluated vaporization enthalpies in combination with gas-phase enthalpies of formation were used for estimation liquid-phase enthalpies of formation of dihalogen-substituted benzenes. Pairwise interactions of halogens on the benzene ring were derived and used for development of simple group additivity procedures for estimation of vaporization enthalpies, gas-phase, and liquid-phase enthalpies of formation of dihalogen-substituted benzenes.

1. INTRODUCTION

Design and operation of chemical and biochemical processes is based on the knowledge of reliable physical and chemical properties of pure compounds, such as enthalpies of vaporization, fusion, and formation. However, experimental data available in the literature since the first thermochemical experiments by Lavoisier are often of questionable quality due to an insufficient purity of samples or inaccurate methods used. Thus, development of any data evaluation methods is highly required. Physical, chemical, and thermodynamic properties of organic compounds are generally connected to their structures and vary with them in a systematic way. That is why identification of any qualitative and quantitative correlations between structure and property is very helpful for the data evaluation, as well as for the prediction of properties of new molecules. While the chemical industry offers about 1000 new compounds each year, it is hopeless to expect to have measured thermochemical data on these compounds. Following it is essential to develop accurate methods to predict

them, but prediction methods have to be based on reliable experimental data.

There is no lack of empirical, half-empirical, and theoretical methods for prediction of thermochemical properties.[1−5] One of the widely used empirical methods is the group-contribution method, where the property of a compound is estimated as a summation of the contributions of simple chemical groups, which can occur in the molecular structure.[1] This method provides accurate prediction of thermochemical properties for a broad range of organic compounds.[4,5] However, recent developments in the field of computational chemistry are now in competition with empirical methods. First-principles methods promise to calculate enthalpies of formation in the gas phase, $\Delta_f H_m^\circ(g, 298.15 \text{ K})$, with a "chemical accuracy" of (2 to 4) kJ mol^{-1} by using composite methods.[5,6] We share this optimism and also believe that the combination of the quantum

chemistry methods with the group-additivity procedure could open a new window of opportunity to elaborate specific group contributions previously not available because of missing experimental data. The combination of the quantum chemistry methods with the experimental vaporization (or sublimation) enthalpies suggests a rational, indirect way[6,7] to obtain not only enthalpies of formation in the gas state, but also values of $\Delta_f H_m^{\circ}$(liq, 298.15 K) and $\Delta_f H_m^{\circ}$(cr, 298.15 K) in the condensed state which are in demand in the thermochemical literature.

The present work is part of a broader program, aiming at the evaluation of experimental data and the development of empirical and theoretical prediction methods. In contrast to the traditional overall group-additivity methodology developed for the broad range of organic compounds,[1−5] we prefer to focus our efforts rather on special families of chemical compounds where structure−property relations are apparent, e.g., homologous series[4,8,9] or substituted benzenes.[7,10] The aim of this paper is to reveal structure−property regularities in *ortho*-, *meta*, and *para*-dihalogen-substituted benzenes (with F, Cl, Br, and I) in order to get a consistent set of enthalpies of vaporization and enthalpies of formation in the gas and liquid phases for these compounds. The latter values are intended to derive pairwise interactions of halogens on the benzene ring, which are expected to be transferable to atmosphere pollutants like polyhalogenated biphenyls, dioxins, and so forth. The study of mixed halogenated pollutants is currently a cutting edge topic in environmental chemistry. The prediction of thermochemical properties for mixed halogenated benzenes based on the results of this work is a valuable contribution in this context.

2. EXPERIMENTAL SECTION

2.1. Materials. Samples used in this work were of commercial origin (see Table S1, Supporting Information). Prior to experiments, samples were purified by repeated vacuum fractional distillation with the Teflon spinning-band column under reduced pressure. Solid samples were purified by fractional sublimation under reduced pressure. Sample purities were determined by using a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector. No impurities (greater than mass fraction 0.001) could be detected in the samples used for the thermochemical measurements (see Table S1, Supporting Information).

2.2. Vapor Pressure Measurements with the Transpiration Method. The transpiration method has been successfully developed in our lab for measurements of vapor pressures of 500−7000 Pa and downward.[11−13] This method is particularly practical for compounds of a middle and low volatility at the temperatures around 298 K, where the data are especially relevant for text books and compilations. About 0.5 to 1 g of the pure sample was mixed with glass beads and placed in a U-shaped saturator having a length of 20 cm and a diameter of 0.5 cm. At a constant temperature (±0.1 K), a nitrogen stream was passed through the saturator at an appropriate flow rate, which was selected to be sufficient for saturation of the stream with the sample. An exactly defined nitrogen stream was passed through the saturator within a certain time and the transported material was trapped at 243 K. The mass of the condensed sample was derived by GC using the external standard method.

The absolute vapor pressure p_i at each temperature T_i was calculated from the amount of the product collected within a definite period of time assuming validity of the ideal gas law, as well as the validity of Dalton's law applied to the nitrogen stream saturated with the substance *i*:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i \quad V = V_{N2} + V_i \quad (V_{N2} \gg V_i) \qquad (1)$$

where R = 8.314472 J·K^{-1}·mol^{-1}; m_i is the mass of the condensed compound, M_i is the molar mass of the compound *i*, and V_i is its volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas, and T_a is the temperature of the flow rate sensor. The volume of the carrier gas V_{N2} was determined by the digital flow rate sensor from integration with a microcontroller. It has turned out that a typical accuracy of vapor pressures measured by transpiration method was within 1−3% and it was governed mostly by two factors: the reproducibility of the GC analysis as well as by the volume V_{N2} determination.[7,10−13]

The saturated vapor pressures p_i measured at different temperatures were fitted with the following equation:[11,12]

$$R \cdot \ln p_i = a + \frac{b}{T} + \Delta_l^g C_p \cdot \ln\left(\frac{T}{T_0}\right) \qquad (2)$$

where a and b are adjustable parameters, and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous phase, C_p^g, and the liquid phase, C_p^l, respectively. The temperature T_0 appearing in eq 2 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, vaporization enthalpy at temperature T was indirectly derived from the temperature dependence of vapor pressures using eq 3:

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p \cdot T \qquad (3)$$

Values of C_p^g have been calculated by using the G4 method (see Table 1). Values of C_p^l were either available from the literature or calculated by the group-contribution procedure developed by Chickos and Acree[14] (see Table 1). Equations 1−3 are also valid for the study of the solid samples. For this case, the enthalpy of sublimation was derived from eq 3 by using the appropriate values of C_p^{cr} and $\Delta_{cr}^g C_p$ (see Table 2) derived in the same way as for the liquid samples. Primary experimental results and the parameters a and b are listed in Table 3A−D. The procedure for calculation of the combined uncertainties of the vaporization enthalpy is described elsewhere.[7] They include uncertainties from the transpiration experimental conditions, uncertainties of vapor pressure, and uncertainties from temperature adjustment to T = 298.15 K.

2.3. Computational Details. Quantum chemical calculations were performed with the Gaussian 09 series of programs.[15] The energies of the compounds under study were calculated using the Gaussian-4 method.[16] The G4 method was chosen as it represents a good compromise between cost and accuracy for substituted benzenes studied in this work.[17] Enthalpy values at the reference temperature H_{298} were evaluated according to the standard thermodynamic procedures.[18]

3. RESULTS AND DISCUSSION

3.1. Vapor Pressure and Vaporization Enthalpies. Experimental absolute vapor pressures of 12 dihalogen-substituted benzenes at different temperatures are given in Table 3A−D. They are compared graphically (see Supporting Information Figures S1−S6). It turned out that vapor pressures of the *para*-isomers in all series were systematically higher in

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Table 1. Compilation of Data on Molar Heat Capacities (in J mol^{-1} K^{-1}) at 298.15 K of the Liquid Dihalogen−Benzenes

compound	$C^{\circ}_{p,m}(liq)$	$C^{\circ}_{p,m}(g)^a$	$\Delta^g_l C_p$	ref.
1,2-difluorobenzene	159.0	104.66	54.3	24
1,3-difluorobenzene	159.11	104.67	54.4	25
1,4-difluoorobenzene	157.5	104.73	52.8	26
1,2-dichlorobenzene	171.3	111.92	59.4	27
1,3-dichlorobenzene	170.6	112.29	58.3	
1,4-dichlorobenzene	179.4	112.25	67.2	
1-bromo-2-chlorobenzene	176.9	113.71	63.2	28
1-bromo-3-chlorobenzene	181.9	114.03	67.9	
1-bromo-4-chlorobenzene	183.2	113.99	69.2	
1-chloro-2-iodobenzene	187.7	114.96	72.7	
1-chloro-3-iodobenzene	187.7	115.24	72.5	
1-chloro-4-iodobenzene	187.7	115.30	72.4	
1-bromo-2-iodobenzene	191.5	116.88^b	74.6	
1-bromo-3-iodobenzene	191.5	117.17^b	74.3	
1-bromo-4-iodobenzene	191.5	117.16^b	74.3	
1,2-dibromobenzene	187.0	115.52	71.5	
1,3-dibromobenzene	187.0	115.76	71.2	
1,4-dibromobenzene	187.0	115.77	71.2	
1-iodo-2-fluorobenzene	173.1	110.96^b	62.1	
1-iodo-3-fluorobenzene	173.1	111.60^b	61.5	
1-iodo-4-fluorobenzene	173.1	111.62^b	61.5	
1,2-diiodobenzene	196.0	117.89^b	78.1	
1,3-diiodobenzene	196.0	117.96^b	78.0	
1,4-diiodobenzene	196.0	118.11^b	77.9	

^{a}Calculated using G4. ^{b}Calculated using b3lyp/6-311G(d,p).

Table 2. Compilation of Data on Molar Heat Capacities (in J mol^{-1} K^{-1}) at 298.15 K of the Solid Dihalogen−Benzenes

compounds	$C^{\circ}_{p,m}(cr)$	$C^{\circ}_{p,m}(g)^a$	$\Delta^g_{cr} C_p$	ref.
1,4-dichlorobenzene	143.8	112.25	31.5	29
1-bromo-4-chlorobenzene	145.5	113.99	31.5	30
1-chloro-4-iodobenzene	149.2	115.30	33.9	30
1-bromo-4-iodobenzene	147.3	117.16	30.1	
1,4-dibromobenzene	145.3	115.77	29.5	29
1,4-diiodobenzene	160.8	118.11^b	42.7	31

^{a}Calculated using G4. ^{b}Calculated using b3lyp/6-311G(d,p).

comparison to the *ortho*-isomers. Vapor pressures of all *meta*-isomers were in between, but in most cases very close to those of the *para*-isomers. Similar trends have already been observed for the halogen substituted methyl-benzenes.[7] Thus, vapor pressures of dihalogen-substituted benzenes measured in this work by transpiration can be considered internally consistent. We also collected the available literature for dihalogen benzenes, systematically treated experimental data using eqs 2 and 3 (with $\Delta^g_l C_p$ and $\Delta^g_{cr} C_p$ values listed in Tables 1 and 2) and calculated values of $\Delta^g_l H_m$ (298.15 K) and $\Delta^g_{cr} H_m$(298.15 K) for the sake of comparison with our results, as well as for the evaluation of the data aiming at the recommendation of vaporization/sublimation enthalpies for further thermochemical calculations. The compilation of vaporization/sublimation enthalpies for dihalogen-substituted benzenes is presented in Table 4. However, not many vapor pressure measurements on dihalogen-substituted benzenes have been found in the literature. A very consistent set of direct (calorimetric) and indirect (from the vapor pressure temperature dependence) measured vaporization enthalpies was reported for dichlorobenzenes.[19] Our own measurements on 1,3-dichlorobenzene

were performed rather in order to reveal any possible peculiarities working with the volatile dihalogen-benzenes with the transpiration method. Our new $\Delta^g_l H_m$ (298.15 K) result for 1,3-dichlorobenzene was in a good agreement with those evaluated in ref 19 (see Table 4). For our discussion of the experimental data we assumed the previous results for vapor pressures and vaporization enthalpies for all three dichlorobenzenes[19] as carefully evaluated. We also used results from our previous data evaluations for *ortho-*, *meta-*, and *para-*isomers of fluoro-chlorobenzenes[20] and dibromobenzenes.[21] Comparison with data collected in the comprehensive compilations by Stephenson and Malanowski[22] and Stull[23] should be considered questionable, because the origin of data, methods of measurements, and uncertainties were not reported there, and purities of compounds were not available. However, in most cases an acceptable agreement of our new results and the literature data has been observed (see Table 4). In order to establish more confidence, we calculated the weighted average values $\Delta^g_l H_m$ (298.15 K) for dihalogen-substituted benzenes under study. Uncertainties of the data were used as the weighting factor. These averaged results were recommended for further thermochemical calculations.

According to our new transpiration results, enthalpies of vaporization of *ortho-*, *meta-*, and *para-*isomers within each series of dihalogen-substituted benzenes were very similar and their differences do not exceed 1 kJ mol^{-1}. Similar trends were also observed for enthalpies of vaporization of halogen-substituted methylbenzenes[7,20] recently.

3.2. Internal Consistency of the Phase Change Enthalpies of 1,4-Dihalogen−benzenes. Fundamental studies on sublimation and fusion of 1,4-dihalogen-substituted benzenes were performed in the Chemical Thermodynamics Group of the Utrecht University[29,30,36] using the static and effusion methods, and adiabatic calorimetry. Sublimation enthalpies for 1-bromo-4-chlorobenzene, 1-iodo-4-chlorobenzene, and 1-bromo-4-iodobenzene measured by the transpiration method in this work were in good agreement with those from the static and effusion methods. However, having the focus of this work on vaporization enthalpies of dihalogen−benzenes, we have additionally measured vapor pressures also over the liquid samples.

A valuable test of consistency of the experimental data on vaporization, and sublimation enthalpies derived for dihalogen−benzenes (see Tables 3A−D and 4) provides a comparison with the experimental values of enthalpy of fusion collected in Table 5. For example, in this work the sample of 1-bromo-4-iodobenzene was investigated by the transpiration method in both ranges, above and below its temperature of melting T_{fus} = 363.3 K. The value of $\Delta^g_{cr} H_m$(298 K) = (76.7 ± 0.3) kJ mol^{-1} for 1-bromo-4-iodobenzene was obtained in this work from measurements in the temperature range 299.4−358.8 K and the vaporization enthalpy for 1-bromo-4-iodobenzene $\Delta^g_l H_m$ (298 K) = (59.8 ± 0.7) kJ mol^{-1} from measurements in the temperature range 366.5−391.6 K. To test the consistency of the experimental data measured in this work for 1-bromo-4-iodobenzene, let us compare the enthalpy of fusion calculated as the difference $\Delta^l_{cr} H_m$(298.15 K) = $\Delta^g_{cr} H_m$ − $\Delta^g_l H_m$ = 76.7−59.8 = (16.9 ± 0.8) kJ mol^{-1} (both values were adjusted to the reference temperature T = 298.15 K) with the $\Delta^l_{cr} H_m$(298.15 K) = (17.2 ± 0.3) kJ mol^{-1} of 4-bromo-iodobenzene reported in ref 28 (see Table 5). The enthalpy of fusion $\Delta^l_{cr} H_m$ calculated from difference the ($\Delta^g_{cr} H_m$ − $\Delta^g_l H_m$) measured in this work is in excellent agreement with those

Table 3A. Results from Measurements of the Vapor Pressure p of Dihalogen-Substituted Benzenes Using the Transpiration Method

T^a	m^b	$V_{(N2)}{}^c$	gas-flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m / \Delta_{cr}^g H_m$
K	mg	dm³	dm³/h	Pa	Pa	kJ mol⁻¹

1,3-Dichlorobenzene: $\Delta_f^g H_m (298.15 \text{ K}) = (52.3 \pm 0.5) \text{ kJ mol}^{-1}$

$$\ln(p/\text{Pa}) = \frac{263.45}{R} - \frac{64726.15}{R\cdot(T,K)} - \frac{58.3}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas-flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m / \Delta_{cr}^g H_m$
278.3	3.27	0.861	2.551	66.5	0.3	48.50
281.3	3.64	0.764	2.551	82.6	−0.2	48.33
284.3	4.09	0.683	2.551	102.7	−0.1	48.15
287.3	4.38	0.597	2.551	125.4	−1.8	47.98
290.3	4.75	0.515	2.551	156.7	0.2	47.80
293.3	4.93	0.428	2.551	195.0	3.4	47.63
296.3	4.82	0.347	2.551	234.8	1.4	47.45
299.3	4.31	0.255	2.551	284.6	1.5	47.28
302.3	4.34	0.219	2.551	333.2	−8.5	47.10
305.3	5.30	0.217	2.551	410.7	0.0	46.93
308.3	6.57	0.222	2.551	496.8	5.3	46.76
311.3	7.66	0.219	2.551	585.1	−0.6	46.58

1-Bromo-2-chlorobenzene: $\Delta_f^g H_m(298.15 \text{ K}) = (52.0 \pm 0.3) \text{ kJ mol}^{-1}$

$$\ln(p/\text{Pa}) = \frac{273.04}{R} - \frac{70813.51}{R\cdot(T,K)} - \frac{63.2}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas-flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m / \Delta_{cr}^g H_m$
280.6	3.41	2.333	3.499	19.28	0.30	53.08
283.7	3.34	1.808	3.499	24.26	−0.08	52.89
286.7	3.89	1.633	3.499	31.06	0.30	52.70
289.6	4.60	1.575	3.499	37.98	−0.39	52.51
291.4	3.56	1.050	3.499	44.04	0.14	52.40
294.2	6.15	1.458	3.499	54.85	0.93	52.22
296.5	2.99	0.618	1.059	62.75	−0.87	52.08
299.6	5.67	0.935	1.059	78.33	−0.81	51.88
302.5	3.26	0.441	1.059	95.48	−1.12	51.70
305.6	3.75	0.406	1.059	119.36	0.40	51.50
308.8	4.13	0.371	1.059	143.64	−3.07	51.30
311.6	5.00	0.371	1.059	173.58	−1.94	51.12
314.5	6.28	0.388	1.059	208.45	−2.04	50.94
317.5	5.24	0.265	1.059	255.21	2.25	50.75
320.5	6.74	0.284	1.064	307.66	4.91	50.56
323.5	6.05	0.213	1.064	368.02	6.08	50.37

1-Bromo-3-chlorobenzene: $\Delta_f^g H_m (298.15 \text{ K}) = (51.3 \pm 0.4) \text{ kJ mol}^{-1}$

$$\ln(p/\text{Pa}) = \frac{277.12}{R} - \frac{71562.71}{R\cdot(T,K)} - \frac{67.9}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T^a	m^b	$V_{(N2)}{}^c$	gas-flow	p^d	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m / \Delta_{cr}^g H_m$
278.2	8.57	5.929	3.909	19.43	0.26	52.68
281.0	3.38	1.759	3.909	25.53	1.49	52.49
283.6	4.18	1.923	3.846	28.07	−1.46	52.31
285.3	3.87	1.538	3.846	33.10	−0.60	52.19
286.1	5.65	2.115	3.846	35.34	−0.50	52.14
289.2	4.25	1.218	3.846	44.94	−0.37	51.93
290.8	5.20	1.346	3.846	50.44	−0.78	51.82
293.9	5.40	1.090	3.846	64.82	0.65	51.61
296.6	5.73	0.977	1.066	75.69	−1.79	51.43
297.0	4.69	0.769	3.846	79.52	−0.17	51.40
299.7	4.59	0.604	1.066	98.16	2.07	51.22
299.9	5.29	0.705	3.846	97.46	0.04	51.20
302.7	4.29	0.462	1.066	119.76	2.00	51.01
303.3	6.08	0.641	3.846	122.30	−0.69	50.97
305.3	4.11	0.368	1.051	142.17	2.25	50.84
305.3	4.94	0.438	1.051	143.81	3.90	50.84
308.2	4.29	0.315	1.051	173.33	4.46	50.64
308.9	8.51	0.641	3.846	170.89	−5.73	50.59
311.3	6.54	0.403	1.051	207.39	1.85	50.43
314.3	6.10	0.315	1.051	247.52	0.05	50.23
317.3	5.69	0.245	1.051	296.62	−0.06	50.02
320.3	6.19	0.228	1.051	347.53	−6.71	49.82

[a]Saturation temperature ($u(T) = 0.1$ K). [b]Mass of transferred sample m condensed at $T = 243$ K. [c]Volume of nitrogen ($u(V) = 0.005$ dm³) used to transfer m ($u(m) = 0.0001$ g) of the sample. [d]Vapor pressure at temperature T calculated from the m and the residual vapor pressure at $T = 243$ K. [e]The combined standard uncertainty of vapor pressures measurements estimated to be within $u(p)/p = (2 \text{ to } 3)$ %, taking into account uncertainties of all variables involved in eq 2. Uncertainties of vaporization enthalpies are expressed in this table as standard deviations.

measured directly by calorimetry (and adjusted to $T = 298.15$ K, as described in Supporting Information). Thus, our new results for vaporization and sublimation enthalpies of 1-bromo-4-iodobenzene have been proven to be consistent. In the same way we tested the experimental results for another dihalogen–benzenes (see Table 5), which have been found in agreement within the experimental uncertainties. Thus, our additional measurements on vaporization, sublimation, and fusion enthalpies of dihalogen-substituted benzenes have ascertained the new thermochemical data for these compounds.

3.3. Evaluation of $\Delta_f^g H_m(298.15$ K) of Dihalogen-Benzenes. Enthalpies of vaporization, $\Delta_f^g H_m$ (298.15 K), of all existing dihalogen-substituted benzenes are collected in Table 4. Are these data self-consistent? Structure–property correlations are always a useful tool to establish consistency of the experimental data. For example, correlation of experimental vaporization enthalpies of monohalogen–benzenes, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene, with experimental enthalpies of vaporization of dihalogen–benzenes, 1,2-difluorobenzene, 1,2-dichlorobenzene, 1,2-dibromobenzene, and 1,2-diiodobenzene, is expected to fit a linear

dependences. Indeed, a remarkable line (see Figure S7, Supporting Information) for 1,2-dihalogenbenzenes meets this expectations. Also, very good linear correlations were found for series of 1,3-and 1,4-dihalogen-substituted benzenes (see Figures S8–S9, Supporting Information). These linear relationships can be considered proof of the internal consistency of experimental results on vaporization enthalpies selected in Table 4. Additionally, another two types of structure–property correlations, the group-additivity procedure[4] and the correlation of vaporization enthalpies with the gas-chromatographic Kovat's index, have been used in this work in order to evaluate vaporization enthalpies of halogen-substituted benzenes.

3.3.1. Correlation of $\Delta_f^g H_m$ (298.15 K) of Dihalogen-Substituted Benzenes with Kovat's Indices. Kovat's indices measured by the gas–liquid chromatography are widely used for identification of molecules,[37] but they also help to reveal structure–property relations within series of parent compounds.[38−40] In our previous studies we found that $\Delta_f^g H_m$ (298.15 K) values appear to be a linear function of the Kovat's indices in homologous series of halogen-substituted ben-

Table 3B. Results from Measurements of the Vapor Pressure p of Dihalogen-Substituted Benzenes Using the Transpiration Method

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m/\Delta_{cr}^g H_m$
K	mg	dm³	dm³/h	Pa	Pa	kJ mol⁻¹

1-Bromo-4-chlorobenzene: $\Delta_{cr}^g H_m(298.15\ K) = (68.1 \pm 0.4)$ kJ mol⁻¹

$$\ln(p/Pa) = \frac{289.99}{R} - \frac{77478.04}{R\cdot(T,K)} - \frac{31.5}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m/\Delta_{cr}^g H_m$
280.1	2.05	4.054	1.919	5.96	−0.34	68.66
283.3	2.04	3.108	1.919	8.44	−0.35	68.56
284.6	2.08	2.554	2.027	10.45	0.41	68.51
286.8	1.67	1.600	2.027	13.35	0.82	68.45
289.8	1.47	1.124	2.043	16.81	−0.06	68.35
292.8	1.40	0.817	2.043	21.87	−0.69	68.26
295.8	1.19	0.511	2.043	29.90	−0.07	68.16
298.5	1.74	0.558	1.312	40.38	1.88	68.08
298.7	1.25	0.411	2.043	38.91	−0.31	68.07
301.7	1.75	0.445	2.043	50.16	−1.35	67.98
302.5	2.15	0.496	1.353	55.89	0.56	67.95
304.8	2.24	0.411	2.055	69.59	1.75	67.88
304.8	2.24	0.411	2.055	69.59	1.75	67.88
307.9	3.60	0.514	2.055	89.48	0.65	67.78
307.9	3.60	0.514	2.055	89.48	0.65	67.78
313.4	4.00	0.371	2.228	138.90	−2.40	67.61
316.5	2.48	0.183	1.098	174.89	−7.28	67.51
319.4	3.30	0.183	1.098	232.60	2.67	67.42
322.6	2.89	0.129	0.776	287.75	−8.00	67.32
325.3	7.09	0.246	0.776	371.87	7.66	67.23
328.6	6.10	0.168	0.776	467.47	0.03	67.13
331.4	9.73	0.220	0.776	570.00	−5.24	67.04
333.1	6.99	0.142	0.776	653.00	1.71	66.99

1-Bromo-4-chlorobenzene: $\Delta_f^g H_m(298.15\ K) = (52.3 \pm 0.6)$ kJ mol⁻¹

$$\ln(p/Pa) = \frac{281.91}{R} - \frac{72915.39}{R\cdot(T,K)} - \frac{69.2}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m/\Delta_{cr}^g H_m$
338.8	32.5	0.405	0.783	1031.9	−16.9	49.47
341.7	17.3	0.183	0.783	1215.6	−1.5	49.27
344.8	17.4	0.157	0.783	1430.6	8.5	49.06
347.7	20.2	0.157	0.783	1657.5	17.8	48.86
350.7	23.2	0.157	0.783	1902.2	7.8	48.65
353.5	44.0	0.261	0.783	2167.0	5.5	48.46

$$\ln(p/Pa) = \frac{281.91}{R} - \frac{72915.39}{R\cdot(T,K)} - \frac{69.2}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m/\Delta_{cr}^g H_m$
356.7	38.5	0.196	0.783	2529.9	24.6	48.24
359.6	34.7	0.157	0.783	2847.9	−7.8	48.03
362.6	44.7	0.176	0.783	3259.6	−1.3	47.83
365.6	44.7	0.157	0.783	3666.9	−46.4	47.62

1-Iodo-2-chlorobenzene: $\Delta_f^g H_m(298.15\ K) = (57.3 \pm 0.3)$ kJ mol⁻¹

$$\ln(p/Pa) = \frac{288.32}{R} - \frac{79001.52}{R\cdot(T,K)} - \frac{72.7}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m/\Delta_{cr}^g H_m$
293.4	1.75	1.569	4.71	11.48	0.14	57.67
295.2	8.09	6.371	5.88	13.17	0.07	57.54
298.3	8.09	4.948	5.94	16.80	0.09	57.32
298.4	2.72	1.647	4.71	16.96	0.12	57.31
301.4	8.09	3.959	5.94	20.97	−0.21	57.09
303.3	3.81	1.608	4.71	24.26	−0.17	56.96
306.7	9.23	2.969	5.94	31.86	0.49	56.71
308.3	7.92	2.353	4.71	34.44	−0.76	56.59
311.9	8.49	1.979	5.94	43.90	−1.49	56.33
313.5	10.66	2.146	4.68	51.18	0.47	56.21
316.3	8.63	1.462	5.85	60.93	−0.43	56.01
318.5	8.32	1.171	4.68	73.17	2.09	55.85
321.4	12.37	1.462	5.85	87.30	1.35	55.64
323.5	11.26	1.210	4.68	95.82	−2.55	55.49
326.3	18.20	1.559	5.85	120.34	2.95	55.28
327.5	7.63	0.637	1.74	123.65	−2.83	55.20
328.3	7.40	0.596	1.19	128.14	−4.75	55.14
331.4	9.09	0.557	1.19	166.63	6.15	54.91
333.4	8.55	0.497	1.19	177.45	−3.38	54.77
336.6	8.60	0.398	1.19	220.78	2.66	54.53
337.5	9.92	0.434	1.74	235.56	5.81	54.47
338.5	9.23	0.397	1.19	239.57	−3.74	54.40
341.4	12.35	0.434	1.74	293.19	6.55	54.19
341.6	8.15	0.301	1.17	279.37	−10.49	54.17
343.5	8.95	0.291	1.17	317.00	−5.08	54.03
345.4	15.52	0.434	1.74	368.46	11.09	53.89

zenes.[7,20] In this study the following empirical equation for the enthalpy of vaporization has been obtained (see Table S2, Supporting Information):

$$\Delta_l^g H_m(298.15\ K)/(kJ\cdot mol^{-1})$$
$$= 9.6 + 0.04 \times J_x(OV\text{-}1)\ \text{with}\ (R^2 = 0.993) \qquad (4)$$

where J_x is the Kovat's index on OV-1[41] of a substituted benzene and R^2 is the correlation coefficient. Also, very good linear correlation of vaporization enthalpies with Kovat's index on SE-30[42] was observed:

$$\Delta_l^g H_m(298.15\ K)/(kJ\cdot mol^{-1})$$
$$= 6.7 + 0.04 \times J_x(SE-30)\ \text{with}\ (R^2 = 0.991) \qquad (5)$$

These relationships can be used to estimate enthalpies of vaporization of the parent substituted benzenes provided that their universal Kovat's indices are known in the same conditions. However, it is more important in the context of the current study that eqs 4 and 5 also be considered as

evidence of internal consistency of the experimental results on vaporization enthalpies evaluated in Table 4.

3.3.2. Group-Contribution Method for Evaluation of $\Delta_f^g H_m$ (298.15 K) of Dihalogen-Substituted Benzenes. Group-additivity (GA) procedure have been systematically applied to the halogen benzenes in our previous work for benzenes substituted with Cl and OH,[43] as well as for CH₃ and F or Cl groups, CH₃, and Br or I groups.[7,20] In this work we extend the GA method for estimation of $\Delta_f^g H_m$ (298.15 K) of dihalogen-substituted benzenes. In short, we developed two types of group contributions. The first type is the contribution due to substitution of the H atom on the benzene ring with any halogen. For example, the difference between $\Delta_f^g H_m$ (298.15 K) of iodobenzene and benzene provides the increment $\Delta H(H \rightarrow I)$ for substitution of H atom on the benzene ring by the I-group. Introduction of the second halogen atom into the benzene ring requires few additional increments, e.g., (ortho I−I), (para I−I), and (meta I−I), taking into account the pairwise interactions of substituents on the benzene ring. A simple general formula was used for calculation of vaporization

Table 3C. Results from Measurements of the Vapor Pressure p of Dihalogen-Substituted Benzenes Using the Transpiration Method

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$/$\Delta_{cr}^g H_m$
K	mg	dm³	dm³/h	Pa	Pa	kJ mol⁻¹

1-Bromo-2-iodobenzene: $\Delta_l^g H_m$(298.15 K) = (59.6 ± 0.3) kJ mol⁻¹

$$\ln(p/Pa) = \frac{289.30}{R} - \frac{81836.83}{R\cdot(T,K)} - \frac{74.6}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$/$\Delta_{cr}^g H_m$
283.3	2.74	14.09	4.972	1.70	0.04	60.71
286.3	2.43	9.695	4.972	2.19	0.02	60.48
289.3	2.35	7.127	4.972	2.88	0.06	60.26
292.5	2.44	5.635	4.972	3.79	0.08	60.02
295.5	9.38	17.65	4.972	4.68	−0.09	59.80
298.2	4.11	6.130	3.117	5.80	−0.14	59.59
301.2	4.30	5.091	3.117	7.31	−0.24	59.37
304.2	3.56	3.325	3.117	9.28	−0.25	59.15
307.3	3.93	2.857	3.117	11.87	−0.19	58.92
310.3	4.59	2.701	3.117	14.68	−0.39	58.69
313.2	3.91	1.818	3.117	18.56	−0.03	58.48
316.4	5.05	1.870	3.117	23.62	0.29	58.24
319.2	4.29	1.299	3.117	28.90	0.58	58.03
322.2	3.98	0.987	3.117	35.24	0.54	57.80
325.4	4.35	0.883	3.117	43.09	0.19	57.57
328.2	4.64	0.779	3.117	52.15	0.73	57.36

1-Bromo-3-iodobenzene: $\Delta_l^g H_m$(298.15 K) = (60.8 ± 0.3) kJ mol⁻¹

$$\ln(p/Pa) = \frac{294.03}{R} - \frac{82958.61}{R\cdot(T,K)} - \frac{74.3}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$/$\Delta_{cr}^g H_m$
279.4	6.38	44.54	3.480	1.27	0.02	62.20
280.4	9.30	59.16	3.480	1.39	0.01	62.13
281.5	8.61	49.76	3.480	1.53	0.00	62.05
284.5	6.66	28.53	3.480	2.06	0.03	61.82
287.8	5.11	16.53	3.480	2.71	−0.02	61.58
289.8	5.13	13.86	3.480	3.25	−0.02	61.43
292.2	4.66	10.09	3.480	4.04	0.01	61.25
292.7	5.55	11.45	3.488	4.24	0.03	61.21
295.4	5.95	9.959	3.880	5.22	−0.07	61.01
298.2	4.33	5.654	1.722	6.68	0.00	60.81
298.4	5.81	7.441	3.488	6.81	0.02	60.79
301.2	5.49	5.629	1.787	8.51	−0.01	60.58
304.4	4.72	3.779	3.488	10.90	−0.09	60.35
306.7	4.86	3.314	3.488	12.77	−0.37	60.17
309.8	4.55	2.442	3.488	16.23	−0.40	59.94
311.3	5.98	2.799	1.768	18.60	0.01	59.83
314.4	5.24	1.974	1.768	23.12	−0.23	59.60
316.7	5.69	1.768	1.768	28.03	0.48	59.43
319.7	5.55	1.385	1.768	34.87	0.83	59.21

$$\ln(p/Pa) = \frac{294.03}{R} - \frac{82958.61}{R\cdot(T,K)} - \frac{74.3}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$/$\Delta_{cr}^g H_m$
322.8	5.36	1.090	1.768	42.74	0.59	58.98

1-Bromo-4-iodobenzene: $\Delta_l^g H_m$(298.15 K) = (59.8 ± 0.7) kJ mol⁻¹

$$\ln(p/Pa) = \frac{291.40}{R} - \frac{81992.02}{R\cdot(T,K)} - \frac{74.3}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$/$\Delta_{cr}^g H_m$
366.5	14.54	0.234	0.877	542.0	1.2	54.76
368.3	13.82	0.205	0.877	588.5	−1.9	54.63
370.2	15.27	0.205	0.877	650.0	1.5	54.49
373.3	13.91	0.161	0.807	750.4	1.2	54.26
375.2	15.11	0.161	0.807	815.4	−3.2	54.12
377.1	17.09	0.168	0.777	883.8	−9.4	53.98
371.7	16.14	0.202	0.807	696.7	1.9	54.38
381.4	20.66	0.164	0.822	1094.0	7.7	53.65
382.3	20.92	0.161	0.807	1128.4	0.4	53.59
378.8	24.40	0.219	0.822	969.3	4.4	53.85
387.4	27.14	0.168	0.777	1403.2	−4.1	53.21
384.9	22.51	0.155	0.777	1260.7	−3.1	53.40
389.4	27.43	0.155	0.777	1536.2	1.2	53.06
391.6	31.20	0.161	0.807	1682.0	2.7	52.90

1-Bromo-4-iodobenzene: $\Delta_{cr}^g H_m$(298.15 K) = (76.7 ± 0.3) kJ mol⁻¹

$$\ln(p/Pa) = \frac{293.24}{R} - \frac{85671.18}{R\cdot(T,K)} - \frac{30.1}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_l^g H_m$/$\Delta_{cr}^g H_m$
299.4	4.75	17.72	5.136	2.35	0.05	76.66
305.2	4.19	8.988	5.136	4.03	−0.10	76.49
308.2	5.90	9.461	0.783	5.37	−0.17	76.40
311.3	4.00	4.537	5.136	7.60	0.15	76.30
314.3	4.34	3.852	5.136	9.72	−0.15	76.21
317.3	4.08	2.739	5.136	12.87	−0.13	76.12
320.4	4.12	2.054	5.136	17.33	0.14	76.03
324.3	4.48	1.592	0.783	24.65	0.43	75.91
328.6	9.74	2.397	5.136	35.17	0.17	75.78
333.4	5.54	0.914	0.783	52.54	0.36	75.64
336.1	4.74	0.626	0.783	65.54	0.58	75.56
339.3	6.54	0.666	0.783	85.35	1.53	75.46
342.2	6.09	0.496	0.783	106.83	1.29	75.37
348.4	5.83	0.300	0.783	168.49	0.11	75.19
351.2	5.53	0.235	0.783	204.36	−2.71	75.10
354.3	5.80	0.196	0.783	257.49	−1.82	75.01
358.8	9.47	0.235	0.783	350.72	−6.09	74.87

enthalpy of any polyhalogen-substituted benzene (HalB) at 298.15 K:

$$\Delta_l^g H_m(HalB) = \Delta_l^g H_m(B) + n_a \times \Delta H(H \rightarrow Hal)$$
$$+ n_b \times (orthoHal - Hal) + n_c \times (metaHal - Hal)$$
$$+ n_d \times (paraHal - Hal) \tag{6}$$

where $\Delta_l^g H_m(B)$ is vaporization enthalpy of benzene; $\Delta H(H \rightarrow Hal)$ is an increment for H → Hal substitutions on the benzene ring, with $n_a = 2$ for disubstituted molecules. The pairwise interactions of the Hal atoms were taken into account through the three types of corrections in *ortho*-, *meta*-, and *para*-positions on the benzene ring, and n_b, n_c, n_d are the quantities of the corresponding increments. This approach is valid for any

kind of polysubstitution of the benzene ring.[43] The same simple substitution procedure can be applied to the toluene, xylenes, polymethyl-benzenes, as well as biphenyls and dioxines using an appropriate shape of the starting molecule, increment ΔH, and eq 6 appropriately modified with the pairwise interactions (see Table 6).

We used the experimental values $\Delta_f^g H_m$ (298.15 K) for benzene and halogen−benzenes available from the literature (see Table 7) together with vaporization enthalpies of dihalogen-substituted benzenes collected in Table 4 in order to derive increments $\Delta H(H \rightarrow Hal)$ and parameters for pairwise interactions of substituents on the benzene ring (see Table 6). These parameters can be used for prediction of vaporization enthalpies of different halogen substituted

Table 3D. Results from Measurements of the Vapor Pressure p of Dihalogen-Substituted Benzenes Using the Transpiration Method

1,2-Diiodobenzene: $\Delta_{cr}^{g}H_{m}(298.15\ K) = (65.6 \pm 0.5)$ kJ mol^{-1}

$$\ln(p/\text{Pa}) = \frac{300.92}{R} - \frac{88928.41}{R\cdot(T,K)} - \frac{78.1}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_{m}/\Delta^{g}H_{m}$
K	mg	dm^3	dm^3/h	Pa	Pa	kJ mol^{-1}
298.5	2.54	12.53	5.921	1.51	0.10	65.62
301.3	2.88	11.55	5.921	1.88	0.07	65.40
304.1	3.19	10.67	5.873	2.23	−0.07	65.18
306.4	3.45	9.495	5.873	2.71	−0.07	65.00
309.7	3.54	7.341	5.873	3.60	−0.05	64.74
312.9	4.80	7.341	5.873	4.88	0.16	64.49
316.4	4.45	5.576	6.196	5.96	−0.25	64.22
319.7	4.65	4.544	6.196	7.76	−0.22	63.96
323.3	4.33	3.201	6.196	10.22	−0.22	63.68
326.9	4.42	2.582	6.196	12.93	−0.61	63.40
330.3	4.30	1.962	6.196	16.46	−0.75	63.14
333.0	5.22	1.875	5.921	20.72	−0.01	62.93
336.0	5.83	1.678	5.921	25.90	0.52	62.69
339.0	5.87	1.382	5.921	31.65	0.69	62.46
341.9	5.69	1.086	5.921	39.08	1.74	62.23
345.0	6.19	0.987	5.921	46.65	1.06	61.98
347.9	6.52	0.888	5.921	54.54	0.15	61.76

1,3-Diiodobenzene: $\Delta_{cr}^{g}H_{m}(298.15\ K) = (66.1 \pm 0.4)$ kJ mol^{-1}

$$\ln(p/\text{Pa}) = \frac{302.46}{R} - \frac{89397.13}{R\cdot(T,K)} - \frac{78.0}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_{m}/\Delta^{g}H_{m}$
K	mg	dm^3	dm^3/h	Pa	Pa	kJ mol^{-1}
312.3	4.21	6.822	5.248	4.60	0.08	65.04
315.4	3.95	5.161	5.248	5.78	0.00	64.80
318.4	4.03	4.198	5.248	7.23	−0.10	64.56
321.2	3.92	3.324	5.248	8.87	−0.19	64.34
324.5	4.39	2.886	5.248	11.48	−0.05	64.09
327.2	3.73	2.012	5.248	14.00	−0.03	63.88
330.3	3.16	1.399	5.248	17.09	−0.39	63.64
309.3	3.97	8.081	5.158	3.61	0.06	65.28
333.2	4.54	1.572	3.930	21.19	−0.19	63.41
336.1	6.35	1.769	3.930	26.37	0.33	63.19
339.0	5.67	1.310	3.930	31.80	0.20	62.96
342.2	5.20	0.983	3.930	39.42	0.50	62.71
345.0	6.31	0.983	3.930	47.84	1.17	62.49
348.3	7.99	1.048	3.930	56.82	−0.52	62.23
351.0	8.24	0.917	3.930	66.97	−0.46	62.02

1,3-Diiodobenzene: $\Delta_{cr}^{g}H_{m}(298.15\ K) = (82.6 \pm 0.6)$ kJ mol^{-1}

$$\ln(p/\text{Pa}) = \frac{321.29}{R} - \frac{95340.36}{R\cdot(T,K)} - \frac{42.70}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_{m}/\Delta^{g}H_{m}$
K	mg	dm^3	dm^3/h	Pa	Pa	kJ mol^{-1}
279.0	1.64	104.9	5.941	0.118	−0.002	83.43
280.9	1.89	93.17	5.941	0.153	−0.001	83.35
284.3	2.35	73.82	5.797	0.238	0.004	83.20
287.0	1.31	30.30	5.941	0.321	−0.004	83.09
288.2	1.22	24.68	5.970	0.368	−0.008	83.04
289.9	1.17	18.74	5.980	0.467	0.006	82.96
292.9	1.53	16.94	5.980	0.676	0.016	82.83
293.9	1.91	18.81	5.970	0.757	0.021	82.79
296.3	1.45	11.01	5.797	0.980	0.010	82.69
299.4	1.98	10.63	5.797	1.391	0.019	82.56
301.8	3.45	14.90	6.040	1.745	−0.041	82.46
303.5	1.58	5.60	5.797	2.093	−0.054	82.38

1,4-Diiodobenzene: $\Delta_{cr}^{g}H_{m}(298.15\ K) = (85.4 \pm 0.4)$ kJ mol^{-1}

$$\ln(p/\text{Pa}) = \frac{314.27}{R} - \frac{98168.24}{R\cdot(T,K)} - \frac{42.7}{R}\ln\left(\frac{T,K}{298.15}\right)$$

T	m	$V_{(N2)}$	gas-flow	p	$(p_{exp} - p_{calc})$	$\Delta_{cr}^{g}H_{m}/\Delta^{g}H_{m}$
K	mg	dm^3	dm^3/h	Pa	Pa	kJ mol^{-1}
298.1	1.64	73.38	5.180	0.170	0.007	85.44
301.2	2.01	63.43	5.014	0.237	0.005	85.31
304.6	1.61	36.27	5.121	0.330	−0.010	85.16
307.3	3.74	60.59	5.014	0.465	0.009	85.05
310.2	1.47	18.22	5.014	0.608	−0.018	84.92
313.1	0.88	8.024	5.349	0.809	−0.040	84.80
316.6	3.27	20.38	5.180	1.211	−0.006	84.65
319.8	5.21	23.09	4.966	1.674	0.004	84.51
322.7	2.45	8.440	5.014	2.162	−0.061	84.39
322.9	8.47	27.40	4.966	2.286	0.020	84.38
325.9	4.09	10.11	5.014	3.027	−0.013	84.25
329.1	5.42	9.861	5.014	4.131	0.019	84.12
332.0	3.92	5.386	4.972	5.447	0.093	83.99
334.9	4.28	4.558	4.972	7.027	0.060	83.87
338.1	4.05	3.232	4.972	9.410	0.146	83.73
341.1	4.01	2.486	4.972	12.094	0.057	83.61
344.1	3.26	1.574	4.972	15.571	0.009	83.48
346.7	2.98	1.160	4.972	19.313	−0.054	83.37

aromatic compounds. Table 6 represents a reasonably minimized number of parameters required for estimation vaporization enthalpies of halogen substituted benzenes. In order to reduce this number most of the minor interactions (having a level below 0.3 kJ mol^{-1}) were neglected or fixed as structure independent constants. For example for all ortho F-(F,Cl,Br,I) interactions a single parameter of 1.5 kJ mol^{-1} was fixed. For all three (Cl−Cl) interactions a single parameter of −1.5 kJ mol^{-1} was also assigned. Moreover, all three (Cl−I) and (Br−Br) interactions were completely neglected. However, some of pairwise interactions, e.g., (Cl−Br), (Br−I), and (I−I) were non-negligible and their small contributions (of few kJ mol^{-1}) to $\Delta_{f}^{g}H_{m}$ (see Table 6) were taken into account. In spite of the deliberate simplification of the estimation procedure, $\Delta_{f}^{g}H_{m}$ (298.15 K) calculations according to eq 6 can be performed with sufficient accuracy. Comparison of the experimental and estimated by GA vaporization enthalpies is

given in Supporting Information Table S4 column 4. As can be seen, the average deviation of experimental and calculated $\Delta_{f}^{g}H_{m}$ (298.15 K) was at the level of 0.2−0.5 kJ mol^{-1} and it was quite comparable with the experimental errors of the most experimental entries in Table 4. Following, values of $\Delta_{f}^{g}H_{m}$ (298.15 K) for the dihalogen-substituted benzenes can be predicted with the acceptable accuracy using eq 6 using the set of basic increments listed in Table 6. Otherwise, the success of prediction with eq 6 could also be considered as evidence of the internal consistency of experimental results on vaporization enthalpies evaluated in Table 4.

3.4. Standard Molar Enthalpies of Formation of Dihalogen−Benzenes. Standard molar enthalpies of formation, $\Delta_{f}H_{m}^{\circ}$, of dihalogen−benzenes in the liquid and crystal states are scarce. Compilation of data available in the literature is given in Table 7. Experimental enthalpies of formation of good quality were available only for difluorobenzenes and

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Table 4. Compilation of Data on Enthalpies of Vaporization, $\Delta_l^g H_m$, and Enthalpies of Sublimation, $\Delta_{cr}^g H_m$, of Dihalogen-Substituted Benzenes

compounds	methods[a]	T-range	$\Delta_{cr}^g H_m / \Delta_l^g H_m$ T_{av}	$\Delta_{cr}^g H_m / \Delta_l^g H_m$[b] 298.15 K	ref
1-chloro-2-fluorobenzene (l)	T	277.5−319.2	44.0 ± 0.2	**44.0 ± 0.3**	20
1-chloro-3-fluorobenzene (l)	T	275.8−319.5	43.1 ± 0.1	**43.0 ± 0.2**	20
1-chloro-4-fluorobenzene (l)	T	277.6−323.5	42.7 ± 0.2	**42.8 ± 0.3**	20
1,2-dichlorobenzene (l)	N/A			**48.8 ± 0.5**	19
1,3-dichlorobenzene (l)	N/A			**47.7 ± 0.5**	19
	T	278.3−311.3	47.6 ± 0.3	47.3 ± 0.5	
1,4-dichlorobenzene (l)				**47.6 ± 0.5**	19
1-bromo-2-chlorobenzene (l)	T	280.6−323.5	51.8 ± 0.2	**52.0 ± 0.3**	
1-bromo-3-chlorobenzene (l)	N/A	252−469	47.0	51.3 ± 3.0	22
	T	278.2−320.3	51.2 ± 0.3	51.3 ± 0.4	
				51.3 ± 0.4[c]	
1-bromo-4-chlorobenzene (cr)	S	298.3−334.7	67.8 ± 0.2	68.3 ± 0.3	32
	Ef	250.0−263.8	70.6 ± 0.1	69.3 ± 0.4	32
	S	294.6−337.6	70.1 ± 0.5	70.6 ± 0.6	33
	T	280.1−333.1	67.9 ± 0.3	68.1 ± 0.4	
				68.7 ± 0.2[c]	
1-bromo-4-chlorobenzene (l)	N/A	305.2−470.1	47.9	53.3 ± 2.0	23
	N/A	333−470	47.6	54.6 ± 3.0	22
	T	338.8−365.6	48.6 ± 0.36	52.3 ± 0.6	
				50.8 ± 0.4[d]	
				51.4 ± 0.4[c]	
1-chloro-2-iodobenzene (l)	T	293.4−345.4	55.9 ± 0.2	**57.3 ± 0.3**	
1-chloro-3-iodobenzene (l)				56.7	
1-chloro-4-iodobenzene (l)	N/A	333.2−443.2	52.2	58.8 ± 3.0	34
	N/A	333−500	50.0	58.6 ± 3.0	22
				55.7 ± 0.4[d]	
				55.8 ± 0.4[c]	
1-chloro-4-iodobenzene (cr)	S	303−323	61.3 ± 0.6	(61.8 ± 0.8)	35
	Ef	259.0−274.0	72.4 ± 0.1	71.3 ± 0.4	32
	S	301.4−323.9	69.5 ± 0.3	70.0 ± 0.5	32
				70.8 ± 0.3	
1,2-dibromobenzene (l)				**54.3 ± 0.9**	21
1,3-dibromobenzene (l)				**54.9 ± 0.6**	21
1,4-dibromobenzene (l)				**54.9 ± 0.5**	21
1-bromo-2-iodobenzene (l)	T	283.3−328.2	59.1 ± 0.2	**59.6 ± 0.3**	
1-bromo-3-iodobenzene (l)	T	279.4−322.8	60.7 ± 0.2	**60.8 ± 0.3**	
1-bromo-4-iodobenzene (l)	T	366.5−391.6	53.9 ± 0.2	59.8 ± 0.7	
				59.4 ± 0.4[d]	
				59.5 ± 0.4[c]	
1-bromo-4-iodobenzene (cr)	Ef	279.0−291.0	79.4 ± 0.1	(79.0 ± 0.6)	32
	S	330.8−354.9	74.5 ± 0.8	75.8 ± 0.9	32
	T	299.4−358.8	75.8 ± 0.2	76.7 ± 0.3	
				76.6 ± 0.3[c]	
1,2-diiodobenzene (l)	T	298.5−347.9	63.8 ± 0.4	**65.6 ± 0.5**	
1,3-diiodobenzene (l)	T	312.3−351.0	63.7 ± 0.3	66.1 ± 0.4	
				67.0 ± 0.7[d]	
				66.3 ± 0.4[c]	
1,3-diiodobenzene (cr)	T	279.0−303.5	82.9 ± 0.5	**82.6 ± 0.6**	
1,4-diiodobenzene (l)	N/A	402−560	51.9	66.1 ± 3.0	22
				66.8 ± 0.7[d]	
				66.8 ± 0.4[c]	
1,4-diiodobenzene (cr)	N/A	372−401	63.4	(67.1 ± 3.0)	22
	T	298.1−346.7	84.4 ± 0.3	**85.4 ± 0.4**	

[a]Methods: Ef = Knudsen effusion method; S = static method; T = transpiration method. [b]Uncertainties in vaporization enthalpies are expressed as standard deviations. Real uncertainties in the literature data were evaluated in this work. Values in brackets were not taken into account. [c]Average values were calculated using the uncertainty of the experiment as a weighing factor. Values in brackets were disregarded by the averaging. Recommended values are given in bold. [d]Calculated as the sum $\Delta_l^g H_m = \Delta_{cr}^g H_m - \Delta_{cr}^l H_m$ (see Table 5).

Table 5. Compilation of Experimental Data on Enthalpies of Fusion, $\Delta_{cr}^{l}H_m$, kJ mol^{-1}

compound	T_{fus}, K	$\Delta_{cr}^{l}H_m$ at T_{fus}	$\Delta_{cr}^{l}H_m{}^a$	$\Delta_{cr}^{g}H_m{}^b$	$\Delta_f^{g}H_m{}^b$	$\Delta_{cr}^{l}H_m{}^c$
				at 298.15 K		
1	2	3	4	5	6	7
1,4-dichlorobenzene	326.1	18.14[28]	17.2 ± 0.2	64.8 ± 0.1[36]	47.6 ± 0.5[19]	17.2 ± 0.5
	326.0	18.16[31]				
1-bromo-4-chlorobenzene	337.9	18.70 ± 0.01[30]	17.3 ± 0.2	68.7 ± 0.2	51.4 ± 0.4	17.3 ± 0.4
	337.8	18.76[28]				
1-chloro-4-iodobenzene	326.7	16.10 ± 0.01[30]	15.1 ± 0.2	70.8 ± 0.3	55.8 ± 0.4	15.0 ± 0.5
1-bromo-4-iodobenzene	363.3	19.61[28]	17.2 ± 0.3	76.6 ± 0.3	59.8 ± 0.7	16.8 ± 0.8
1,3-diiodobenzene	307.4	15.94[28]	15.6 ± 0.2	82.6 ± 0.6	66.1 ± 0.4	16.5 ± 0.7
1,4-diiodobenzene	402.0	22.34[31]	18.6 ± 0.6	85.4 ± 0.4	66.1 ± 3.0	19.3 ± 3.0
	402.2	22.38[28]				

^{a}The experimental enthalpies of fusion $\Delta_{cr}^{l}H_m$ measured at T_{fus} and adjusted to 298.15 K (see Supporting Information). ^{b}Taken from Table 4. ^{c}Calculated as the difference between column 5 and 6 in this table.

Table 6. Parameters for the Calculation of Enthalpies of Vaporization of Dihalogen-Substituted Benzenes at 298.15 K (in kJ mol^{-1})

parameters	$\Delta_f^{g}H_m$	parameters	$\Delta_f^{g}H_m$
benzene	33.9[44]	para F-(F or Cl)	0.4[20]
ΔH(H→F)	0.8[10]	para F-(Br or I)	−0.5
ΔH(H→Cl)	7.9[10]	(Cl−Cl)	−1.5[20]
ΔH(H→Br)	10.4[7]	(Cl−Br)	−0.7
ΔH(H→I)	14.9[7]	(Cl−I)	0.0
ortho F-(F,Cl,Br,I)	1.5[20]	(Br−Br)	0.0
meta F-(F or Cl)	0.0[20]	(Br−I)	1.0
meta F-(Br or I)	−1.0[20]	(I−I)	2.5

dichlorobenzenes, where experiments were performed with the well established rotating bomb combustion calorimetry in laboratories with good experience.[45−47] In contrast, the enthalpy of formation of the solid 1-bromo-4-chlorobenzene was derived from the less reliable reaction calorimetry and the result was reported for the liquid state.[48] In spite of the large uncertainties of 5 kJ mol^{-1} assigned to this value from reaction calorimetry, this result can be considered reliable, because from our experience with other compounds reported in this work, e.g., for 1-bromo-4-methylbenzene, a reasonable value of enthalpy of formation, $\Delta_f H_m^{\circ}$ (liq), was evaluated recently.[7] The enthalpy of formation of the crystalline 1,4-dibromobenzene was recalculated by Stull et al.[49] from the very old data reported by Popoff and Schirokich[51] from combustion calorimetry. The high uncertainty of 4.2 kJ mol^{-1} given for this value corresponds more or less to its reliability. Values $\Delta_f H_m^{\circ}$ (liq or cr) for diiodobenzenes were those recommended by Cox and Pilcher,[50] who derived them from enthalpies of combustion reported by Smith.[52] Thus, this small collection of enthalpies of formation of dihalogen−benzenes in the liquid

Table 7. Thermochemical Data at T = 298.15 K (p° = 0.1 MPa) for Dihalogen-Substituted Benzenes (in kJ mol^{-1})

compounds	$\Delta_f H_m^{\circ}$ (liq or cr) exp.	$\Delta_f^{g}H_m/\Delta_{cr}^{g}H_m$ exp.	$\Delta_f H_m^{\circ}$(g) exp.	$\Delta_f H_m^{\circ}$(g) G4^a	$\Delta_f H_m^{\circ}$(liq)^b
1	2	3	4	5	6
fluorobenzene	−150.8 ± 1.4[45]j	35.0 ± 0.3[10]	−115.8 ± 1.4	−112.6[7]	
chlorobenzene	11.0 ± 1.3[44]	41.8 ± 0.3[10]	52.8 ± 1.3	53.6[7]	
bromobenzene	60.9 ± 4.1[44]	44.5 ± 0.1[7]	105.4 ± 4.1	105.5[7]	
iodobenzene	117.2 ± 4.2[44]	48.9 ± 0.5[7]	166.1 ± 4.2		
1,2-difluorobenzene	−319.2 ± 0.9[26]	36.8 ± 0.2[20]	−282.4 ± 0.9	−295.2	−332.0
1,3-difluorobenzene	−343.9 ± 1.0[26]	35.1 ± 0.2[20]	−308.8 ± 1.0	−311.0	−346.1
1,4-difluorobenzene	−342.3 ± 1.0[26]	36.0 ± 0.2[20]	−306.3 ± 1.0	−307.7	−343.7
1,2-dichlorobenzene	−17.4 ± 1.3[46]	48.8 ± 0.5[19]	31.4 ± 1.4	31.9	−16.9
1,3-dichlorobenzene	−20.5 ± 1.0[47]	47.7 ± 0.5[19]	27.2 ± 1.1	25.9	−21.8
1,4-dichlorobenzene	−25.1 ± 1.1 (liq)^c	47.6 ± 0.5[19]	22.5 ± 1.2	26.6	−21.0
	−42.3 ± 1.0 (cr)[47]	64.8 ± 0.1[36]	22.5 ± 1.0		
1-bromo-4-chlorobenzene	28.0 ± 5.0 (liq)[48]	51.4 ± 0.4	79.4 ± 5.0	79.0	27.6
	10.7 ± 5.0 (cr)^c	68.7 ± 0.2	79.4 ± 5.0		
1,4-dibromobenzene	71.6 ± 4.3 (liq)^c	54.9 ± 0.5[21]	126.5 ± 4.3		76.7
	53.4 ± 4.2 (cr)[49]	74.5 ± 1.1[21]	127.9 ± 4.3	131.6	
1,2-diiodobenzene	187.0 ± 4.2[50]	65.6 ± 0.5	252.6 ± 4.2	259.9^d	194.3
1,3-diiodobenzene	202.6 ± 4.2 (liq)^c	66.3 ± 0.4	268.9 ± 4.2		186.6
	187.0 ± 4.2 (cr)[50]	82.6 ± 0.6	269.6 ± 4.2	252.8^d	
1,4-diiodobenzene	179.3 ± 4.2 (liq)^c	66.8 ± 0.4	246.1 ± 4.2		186.2
	160.7 ± 4.2 (cr)[50]	85.4 ± 0.4	246.1 ± 4.2	253.0^d	

^{a}Calculated using enthalpies H_{298} calculated by G4 (see Table S5, Supporting Information) for the reaction 7 ^{b}Calculated as the difference between columns 5 and 3 in this table. ^{c}Calculated from enthalpy of formation in the condensed state and enthalpy of fusion from Table 5. ^{d}Calculated from enthalpy of formation of iodobenzene (this table) and pairwise interactions from Table 9.

and crystal state together with vaporization/sublimation enthalpies evaluated in Table 4 have been used to calculate the molar standard enthalpies of formation in the gas state (see Table 7, column 4) for comparison with results from quantum-chemical calculations.

3.5. Quantum Chemical Calculations of the Gas-Phase Enthalpies of Formation. Modern quantum chemical methods, especially composite methods, are able to calculate enthalpies of formation, $\Delta_f H_m^\circ$ (g, 298.15 K), of small molecules with a "chemical accuracy"[5,6] of 2–4 kJ mol^{-1}. Dihalogen-substituted benzenes studied in this work seem to be optimal in size to fulfill this expectation.

Isodesmic and homodesmic reactions are conventionally used for converting of quantum chemical calculated energies into enthalpies of formation. These reactions rely upon the similarity of bonding environments in the reactants and products that leads to cancellation of systematic errors in the quantum chemical calculations. The enthalpies of formation of dihalogen-benzenes were calculated via the energies (see Table S5, Supporting Information) of ring-conserved homodesmic reactions:
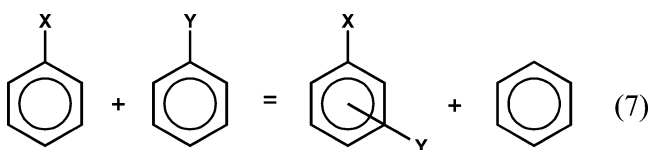
Using enthalpies of reaction 7 calculated by G4 together with enthalpies of formation, $\Delta_f H_m^\circ$ (g), for benzene[44] and halogen-substituted benzenes (see Table 7 and Table 8) enthalpies of formation of all isomeric dihalogen–benzenes have been calculated (see Table 7, column 5). Theoretical enthalpies of formation of *meta*- and *para*-difluorobenzenes, *ortho*- and *meta*-dichlorobenzenes, as well as for 1-bromo-4-chlorobenze are in excellent agreement with the experimental values. Agreement for 1,4-dichloro- and 1,4-dibromobenzenes is still acceptable within the boundaries of experimental uncertainties. Theoretical enthalpies of formation for all three diiodobenzenes significantly disagree with experimental results, even taking into account the large uncertainties of the experiment of 4.2 kJ mol^{-1}. In our opinion the theoretical enthalpies of formation of diiodobenzenes should be considered more consistent and reliable. Much to our surprise, the theoretical value of $\Delta_f H_m^\circ(g)$ for *ortho*-difluorobenzene deviates by 13 kJ mol^{-1} from the experiment. At the same time for the similar shaped *ortho*-dichlobenzene, as well as for *meta*- and *para*-difluorobenzenes agreement between experiment and theory is excellent. Moreover, the G4-method was successfully tested for 38 fluoro- and chloro-containing molecules.[53] Careful reading of the original work by Good et al.[45] did not reveal any deficiency in *ortho*-difluorobenzene sample preparation. It was purified by efficient fractional column, and purity of 99.998 ± 0.002 mol % was determined by calorimetric studies of melting point as a function of the fraction melted. In the framework of the current study we decided to prefer the theoretical enthalpy of formation of *ortho*-difluorobenzene, but we shall pay attention to this disagreement in our future work.

Having in mind the apparent disagreement of theoretical and experimental $\Delta_f H_m^\circ$ (g) for *ortho*-difluorobenzene, it was reasonable to apply any structure−property correlations to establish consistency of the $\Delta_f H_m^\circ$ (g) data. Similar to analysis performed for vaporization enthalpies in section 3.3, we correlated experimental values $\Delta_f H_m^\circ$ (g) of fluorobenzene,

Table 8. Thermochemical Data at T = 298.15 K for Dihalogen−Benzenes (in kJ mol^{-1}) and Pairwise Interactions of Substituents, $\Delta_r H_m^\circ$, on the Benzene Ring for of Dihalogen-Substituted Benzenes as Calculated by the G4 at 298.15 K

compounds	$\Delta_g^g H_m$	$\Delta_r H_m^\circ(g)$	$\Delta_f H_m^\circ(g)/$ G4^a	$\Delta_f H_m^\circ(liq)^b$
1	2	3	4	5
1,2-difluorobenzene	36.8 ± 0.2	19.0	−295.2	−332.0
1,3-difluorobenzene	35.1 ± 0.2	3.2	−311.0	−346.1
1,4-difluorobenzene	36.0 ± 0.2	6.5	−307.7	−343.7
1-chloro-2-fluorobenzene	44.0 ± 0.3	12.1	−133.6	−177.6
1-chloro-3-fluorobenzene	43.0 ± 0.3	3.4	−142.2	−185.2
1-chloro-4-fluorobenzene	42.8 ± 0.3	4.8	−140.8	−183.6
1,2-dichlorobenzene	48.8 ± 0.5	10.6	31.9	−16.9
1,3-dichlorobenzene	47.7 ± 0.5	3.4	25.9	−21.8
1,4-dichlorobenzene	47.6 ± 0.5	4.7	26.6	−21.0
1-bromo-2-fluorobenzene	47.0 ± 0.3	8.9	−82.4	−129.4
1-bromo-3-fluorobenzene	44.3 ± 0.3	2.9	−89.6	−133.9
1-bromo-4-fluorobenzene	44.0 ± 0.4	3.6	−88.3	−132.3
1-iodo-2-fluorobenzene	50.8 ± 0.2	8.6^c	−25.1	−75.9
1-iodo-3-fluorobenzene	48.5 ± 0.2	2.7^c	−26.8	−75.3
1-iodo-4-fluorobenzene	49.6 ± 0.2	3.4^c	−28.4	−78.0
1-bromo-2-chlorobenzene	52.0 ± 0.3	8.7	84.2	32.2
1-bromo-3-chlorobenzene	51.3 ± 0.4	2.6	78.3	27.0
1-bromo-4-chlorobenzene	51.4 ± 0.4	3.4	79.0	27.6
1-chloro-2-iodobenzene	57.3 ± 0.3	7.2^c	145.8	88.5
1-chloro-3-iodobenzene	56.7	5.5^c	139.5	82.8
1-chloro-4-iodobenzene	55.8 ± 0.4	3.9^c	140.4	84.6
1,2-dibromobenzene	54.3 ± 0.9	9.5	136.9	82.6
1,3-dibromobenzene	54.9 ± 0.6	3.2	130.8	75.9
1,4-dibromobenzene	54.9 ± 0.5	4.1	131.6	76.7
1-bromo-2-iodobenzene	59.6 ± 0.3	9.9^c	198.8	139.2
1-bromo-3-iodobenzene	60.8 ± 0.3	3.1^c	192.0	131.2
1-bromo-4-iodobenzene	59.5 ± 0.4	2.5^c	191.4	131.9
1,2-diiodobenzene	65.6 ± 0.5	10.3^c	259.9	194.3
1,3-diiodobenzene	66.3 ± 0.4	3.2^c	252.8	186.5
1,4-diiodobenzene	66.8 ± 0.4	3.4^c	253.0	186.2

^{a}Calculated using enthalpies H_{298} calculated by G4 (see Table S5, Supporting Information) for reaction 7. ^{b}Calculated as the difference between columns 4 and 2 in this table. ^{c}Calculated using correlations between $\Delta_r H_m^\circ$(G4) and between $\Delta_r H_m^\circ$(B3LYP/6-311G(d,p)).

chlorobenzene, bromobenzene, and iodobenzene (see Table 7, column 4) with theoretical enthalpies of formation of 1,2-difluorobenzene, 1,2-dichlorobenzene, 1,2-dibromobenzene, and 1,2-diiodobenzene (see Table 7, column 5). An excellent linear correlation has been obtained as follows:

$$\Delta_f H_m^\circ(\text{g, 1,2-dihalogen-benzene}) = 1.965$$
$$\times\ \Delta_f H_m^\circ(\text{g, halogen}-\text{benzene}) - 69.0$$
$$\text{with } R^2 = 0.9999$$

In the same way we correlated theoretical values for *meta-* and *para-*isomers:

$$\Delta_f H_m^\circ(\text{g, 1,3-dihalogen-benzene}) = 1.999$$
$$\times\ \Delta_f H_m^\circ(\text{g, halogen}-\text{benzene}) - 79.6$$
$$\text{with } R^2 = 0.9999$$

$$\Delta_f H_m^\circ(\text{g, 1,4-dihalogen-benzene}) = 1.989$$
$$\times\ \Delta_f H_m^\circ(\text{g, halogen}-\text{benzene}) - 77.8$$
$$\text{with } R^2 = 0.9999$$

These very good linear relationships can be considered proof of internal consistency of theoretical results on enthalpies of formation calculated by the G4-method.

3.6. Combination of Quantum Chemical Calculations and Evaluated Vaporization Enthalpies for Prediction of the Liquid-Phase Enthalpies of Formation. Having confirmed ability of the G4-method to calculate reliable gas-phase enthalpies of formation of dihalogen-substituted benzenes (see Table 7, column 5), as well as having a self-consistent set of their vaporization enthalpies (see Table 4 and Table 8, column 2) evaluated in the current study, we calculated $\Delta_f H_m^\circ(\text{liq, 298.15 K})$ of dihalogen−benzenes absent in the thermochemical literature using the basic thermodynamic equation:

$$\Delta_f H_m^\circ(\text{liq, 298.15 K}) = \Delta_f H_m^\circ(\text{g, G4}) - \Delta_l^g H_m(\text{exp}) \quad (8)$$

Results are given in Table 7, column 6, and Table 8, column 5. For the sake of comparison we also derived enthalpies of formation of dihalogen−benzenes in the liquid phase using available enthalpies of formation in the crystalline phase (see Table 7) and enthalpies of fusion collected in Table 5. A good agreement of experimental enthalpies of formation and those estimated with eq 8 was found for 1,3-difluorobenzene, 1,4-difluorobenezenes, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 4-bromo-chlorobenzene. The agreement for 1,4-dichlorobenzene and 1,4-dibromobenzene was acceptable within the large experimental uncertainties of 4.2 kJ mol^{-1}. Estimated enthalpies of formation for diiodobenzenes were in disagreement with experimental results, indicating a necessity of new combustion experiments with these substituted benzenes.

3.7. Mutual Interactions of Substituents on the Benzene Ring (Gas Phase, 298.15 K). Mutual interactions of different substituents in their *ortho-*, *meta-*, and *para-*position on the benzene derived according to eq 7 usually determine reactivity of a compound. In contrast to values of enthalpies of formation, intensities of *ortho-*, *meta-*, and *para-*pairwise interactions render themselves to interpretation more easily. From common knowledge, the *meta-* and *para-*pairwise interactions of different substituents on the benzene ring seldom exceed a few kJ mol^{-1}. In contrast, the *ortho-*interactions are often very strong and they are crucially dependent on the size and the nature of substituent. Using a set of G4 calculated enthalpies H_{298} for halogen- and dihalogen-substituted benzenes (see Table S5, Supporting Information) we estimated interactions on the benzene ring directly from

enthalpies H_{298}. For this purpose the well balanced distribution reaction 7 was applied. The enthalpy $\Delta_r H_m^\circ$ of the reaction 7, calculated according to Hess's Law, directly corresponded to energetics of the mutual interaction of halogens on the benzene ring placed in the *ortho-*, *meta-*, or *para-*position. An advantage of quantum chemical calculations of $\Delta_r H_m^\circ$ for benzene derivatives is that substituent effects are estimated directly from enthalpies H_{298} skipping the common step of using $\Delta_f H_m^\circ(\text{g})$ for the participants of reaction 7. Such a trick allows us to obtain pairwise interactions more accurately and lends them to finer interpretation.

The substituent effects in the dihalogen-substituted benzenes under study defined in terms of $\Delta_r H_m^\circ$ of reaction 7 are listed in Table 8, column 3. In accordance with common sense, the mutual interactions of different halogens in *meta-* and *para-*positions were on the level of 3−4 kJ mol^{-1}. However, contrary to reasonable expectation the strongest *ortho-*halogen interactions of 19 kJ mol^{-1} were observed for the case of the two smallest F-substituents. Destabilization of the molecule due to the *ortho-*interaction of F and Cl substituents was already lower (12.1 kJ mol^{-1}). The *ortho-*interaction of two Cl substituents reduced destabilization to 10.6 kJ mol^{-1}. Further combinations of *ortho-*halogen substituents destabilized the molecule approximately at the same level (see Table 8, column 3), which was 10.3 kJ mol^{-1} even for the *ortho-*interaction of two largest I substituents.

Unfortunately, the G4 method was not parametrized for calculation of I-containing molecules. That is why we additionally used the B3LYP/6-311G(d,p) method[54] where all elements F, Cl, Br, and I are included. Pairwise interactions, $\Delta_r H_m^\circ$, of F, Cl, Br, and I in dihalogen-substituted benzenes calculated by DFT are given in Table S6, Supporting Information. It has turned out that both sets of mutual interactions $\Delta_r H_m^\circ$ derived by the G4 and the DFT methods are not directly comparable. However, in our recent work we have shown that the simple linear correlations between the G4 and the DFT results can be established separately for *ortho-*, *meta-*, and *para-*halogen substituted methylbenzenes.[7] We used the similar procedure in this work for the dihalogen-substituted benzenes and correlated values of $\Delta_r H_m^\circ$ derived from the G4 and DFT methods for each combination of halogen substituents (see Table S5, Supporting Information). With these correlations the missing pairwise interactions $\Delta_r H_m^\circ$ of the iodine with the F, Cl, Br, and I substituents in Table 8 were estimated.

Values of pairwise interactions of halogens on the benzene ring listed in Table 8 can be utilized in physical−organic chemistry as a quantitative manifestation of the sterical and the electron-accepting features of substituents. Moreover, values of $\Delta_r H_m^\circ$ derived in this work can also be used for prediction of $\Delta_f H_m^\circ(\text{g, 298.15 K})$ using the similar GA method as described in section 3.3.2 for vaporization enthalpies. With help of $\Delta_f H_m^\circ(\text{g, 298.15 K}) = (82.6 \pm 0.7)$ kJ mol^{-1} for benzene[44] and enthalpies of formation for monohalogen-substituted benzenes (see Table 7, column 4) the appropriate contributions for exchange of the hydrogen with the halogen on the benzene ring $\Delta H(\text{H} \rightarrow \text{F})$, $\Delta H(\text{H} \rightarrow \text{Cl})$, $\Delta H(\text{H} \rightarrow \text{Br})$, and $\Delta H(\text{H} \rightarrow \text{I})$ have been derived (see Table 9). The pairwise interactions listed in Table 8, column 3, can be applied for accurate prediction of $\Delta_f H_m^\circ(\text{g, 298.15 K})$ of dihalogen-substituted benzenes using eq 6 adjusted for gaseous enthalpies of formation. In order to reduce the number of additive parameters we assigned constant contributions (see Table 9)

Table 9. Parameters for the Calculation of Enthalpies of Formation, $\Delta_f H_m^\circ$, in the Gas State of of Dihalogen-Substituted Benzenes at 298.15 K (in kJ mol^{-1})

parameters	$\Delta_f H_m^\circ(g)$	parameters	$\Delta_f H_m^\circ(g)$
benzene	82.6[44]	meta (hal–hal)	3.0
ΔH(H→F)	−198.4	para (hal–hal)	4.0
ΔH(H→Cl)	−29.8	ortho (F–Cl)	12.1
ΔH(H→Br)	22.8	ortho (F–Br)	10.6
ΔH(H→I)	83.5	ortho (F–I)	7.2
ortho (F–F)	19.0	ortho (Cl–Br)	8.6
ortho (Cl–Cl)	8.9	ortho (Cl–I)	9.5
ortho (Br–Br)	8.7	ortho (Br–I)	9.9
ortho (I–I)	10.3		

to all *meta* and *para* interactions. But even with this simplification, the GA method predicted enthalpies of formation $\Delta_f H_m^\circ$(g, 298.15 K) with very good agreement with those from the experiment and quantum chemical calculations (Supporting Information Table S4, column 7).

3.8. Prediction of Enthalpies of Formation $\Delta_f H_m^\circ$(liq, 298.15 K) of Dihalogen–Benzenes in the Liquid Phase. Enthalpies of formation in the liquid phase, $\Delta_f H_m^\circ$(liq, 298.15 K), were derived in this work by combination of quantum chemical calculations and evaluated vaporization enthalpies (see Table 7, column 6, and Table 8, column 5). These values are often useful in chemical engineering calculations. Having established the consistent set of liquid-phase enthalpies of formation for dihalogen-substituted benzenes, it has been reasonable to derive mutual interactions of halogen substituents on the benzene ring in the liquid phase, in order to apply these interactions to prediction of $\Delta_f H_m^\circ$(liq, 298.15 K). Using the $\Delta_f H_m^\circ$(liq, 298.15 K) = 49.0 ± 0.5 kJ mol^{-1} for benzene[44] and enthalpies of formation for monohalogen-substituted benzenes (see Table 7, column 2), the appropriate contributions ΔH(H→F), ΔH(H→Cl), ΔH(H→Br), and ΔH(H→I) in the liquid phase have been derived (see Table 10). Quantities

Table 10. Parameters for the Calculation of Enthalpies of Formation, $\Delta_f H_m^\circ$, in the Liquid State of Dihalogen-Substituted Benzenes at 298.15 K (in kJ mol^{-1})

parameters	$\Delta_f H_m^\circ$(liq)
benzene	49.0[44]
ΔH(H→F)	−199.8
ΔH(H→Cl)	−38.0
ΔH(H→Br)	11.9
ΔH(H→I)	68.2
ortho (F–F)	18.6
ortho (hal–hal)[a]	8.9
meta and para (hal–hal)[b]	5.0
meta and para (Hal–Hal)[c]	2.0

[a] Except for ortho (F–F). [b] For *meta* and *para* interactions (F–F); (F–Cl); (F–Br); (F–I); (Cl–Cl); (Cl–Br); (Cl–I). [c] For *meta* and *para* interactions (Br–Br); (Br–I); (I–I).

of the *ortho*-, *meta*-, and *para*-effects of substituents on the benzene ring in the liquid phase were derived as the difference between $\Delta_f H_m^\circ$(liq, 298.15 K) listed in Table 8, column 5, and the sum of contributions ΔH(H→Hal) for each type of the dihalogen substitution from Table 10. It has turned out that *ortho*-pairwise interactions in the liquid phase follow in size approximately the same trends as in the gas phase. The largest

ortho interaction of 18.6 kJ mol^{-1} was observed for F substituents. Other *ortho*-effects were mostly at the level of 7−9 kJ mol^{-1} independent of the size and nature of the halogen. Pairwise interactions of different halogens in the *meta*- and *para*-postions were also similar to those in the gas phase, and they stand on the common level of 3−4 kJ mol^{-1}. In order to keep the number of group-additivity contributions to a minimum, we again deliberately neglected fine differences in effects and averaged the pairwise interactions as far as possible. These averaged pairwise interactions were considered a set of empiric constants which are listed in Table 10, and they can be used now for estimation of $\Delta_f H_m^\circ$(liq, 298.15 K) of similarly shaped halogen−benzenes.

To sum up, three sets of thermochemical properties $\Delta_l^g H_m^\circ$(298.15 K), $\Delta_f H_m^\circ$(g, 298.15 K), and $\Delta_f H_m^\circ$(liq, 298.15 K) of dihalogen-substituted benzenes have been derived and evaluated for internal consistency in the framework of this study. Simple group additivity schemes have been developed for all three properties. In spite of the simplicity of the suggested schemes, they are able to predict enthalpies of vaporization and formation with sufficient accuracy comparable with uncertainties of the experimental data used for development of group contributions (see Table S4, Supporting Information). Our current and future work is focused on the extension of the GA procedure to benzenes substituted with COOH, OH, OCH$_3$, CN, NO$_2$, and so forth. Moreover, we are looking for the possibility to transfer values of pairwise interactions for prediction of thermochemical properties of halogenated polyaromatic compounds, biphenyls, dibenzodioxins, or dibenzofurans.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details; additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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