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# Energetics of substituent effects on the benzene ring: $CH_3O$ with F, Cl, Br, and I

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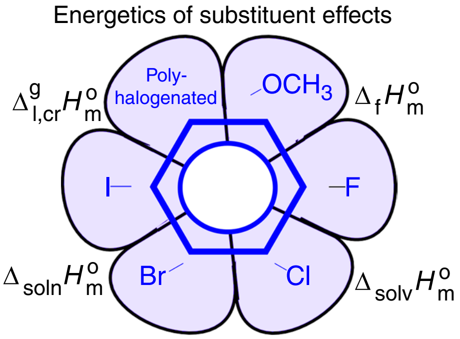
## Abstract

The temperature dependences of vapour pressures for some *mono*- and *di*-halogenated anisoles were established using the transpiration method. The solution calorimetry-based approach was used to determine the vaporization/sublimation enthalpies of chlorine- and iodine-substituted anisoles. The enthalpies of fusion of 2,3-*di*-chloro-anisole and 4-iodo-anisole were measured using differential scanning calorimetry. The literature thermochemical data for halogen-substituted anisoles (with halogen = F, Cl, Br, and I) and new results were evaluated using "structure–property" correlations and quantum-chemical calculations. The G* quantum chemical methods were validated for reliable estimation of the enthalpies of formation of substituted for halogen-substituted anisoles in the gaseous state. The evaluated thermodynamic data were used for designing the "centrepiece" method for assessment of enthalpies of vaporization and enthalpies of formation for halogen-substituted anisoles.

### Graphical abstract



**Keywords** Vapour pressure · Enthalpy of vaporisation · Enthalpy of formation · Structure–property relationships · Quantum-chemical calculations · Group-additivity

## Introduction

Quantitative substituent effects on the benzene ring various functional groups are useful for the quick evaluation or validation of experimental results of phase transition enthalpies. The combination of the experimental enthalpies of formation in the condensed state and the experimental enthalpies of vaporisation/sublimation provides the standard molar enthalpies of formation in the gas phase, which are used to derive the intramolecular effects of substituents. In

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our recent works [1–3], we have also used the gas-phase quantum chemical calculations for benzene derivatives to establish the consistency of the new and available experimental results on vaporisation enthalpies.

The use of experimental and theoretical calculation procedures allows obtaining reliable data that can be used for practical thermochemical calculations. In addition, such data can be used for development of simple calculation procedures for enthalpy of formation in gas phase [4] and solvation enthalpies in various solvents at 298.15 K [5–7]. These thermochemical values at the reference temperature $T = 298.15$ K can easily be adjusted to the temperatures of the real industrial process using the Kirchhoff equation. It is often observed that the enthalpies of vaporisation of isomeric *poly*-halogenated benzenes are very close (within 1 kJ mol$^{-1}$), independent of the position of the substituents on the aromatic ring. As example, the enthalpies of vaporisation at 298.15 K of 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-*tetra*-fluoro-benzenes are 37.5 [8], 36.0 [8], and 37.2 kJ mol$^{-1}$ [8], respectively. Such a similarity is also observed for the vaporisation enthalpies at 298. 15 K of isomeric *tetra*-chloro-benzenes: 1,2,3,4-*tetra*-chloro-benzenes (60.1 kJ mol$^{-1}$ [9]) and 1,2,4,5 -*tetra*-chloro-benzenes (60.7 kJ mol$^{-1}$ [9]). Nevertheless, significant differences can be observed for compounds capable of intramolecular hydrogen bonding, for example, the enthalpies of vaporisation at 298.15 K of 2-bromo-phenol (55.5 ± 1.3 kJ mol$^{-1}$ [10]) and 4-bromo-phenol (68.7 ± 0.1 kJ mol$^{-1}$ [11]) differ by 13.2 kJ mol$^{-1}$. The reason for this is a competition between intramolecular and intermolecular hydrogen bonds, which is responsible for a significantly lower value of the vaporisation enthalpy of the *ortho*-isomer. While developing a new method for determining the vaporisation and sublimation enthalpy of aromatic compounds using solution calorimetry [6], we noticed that the literature data on the vaporisation enthalpies at 298. 15 K of 2,4-*di*-chloro-anisole (62.8 ± 1.5 kJ mol$^{-1}$ [12]) and 2,6-*di*-chloro-anisole (56.1 ± 1.5 kJ mol$^{-1}$ [12]) are unexpectedly different from the compounds that cannot form intramolecular hydrogen bonds. This observation has prompted the systematic study of halogenated anisoles with the intention of uncovering and explaining possibly unusual substituent effects in this series.

## Experimental

### Materials

Most of the compounds used in this work were of commercial origin (see Table S1, electronic supporting information). For this work, the 4-iodo-anisole and 2,4-*di*-iodo-anisole were prepared by iodination of anisole in a round bottom flask equipped with a reflux condenser, dropping funnel and stirrer. Synthesis details are given in the supporting material. Purities were determined using a gas chromatograph equipped with a flame ionization detectors and capillary column of DB-1 with length 50 (Hewlett Packard HP 5890, USA in Rostock) and HP-5 with length 30 m (Agilent 7820 A, USA in Kazan). The purity of all samples was 98–99% (see Table S1). The commercial samples were used for vapour pressure measurements without additional purification. However, before starting the vapour pressure measurements using the transpiration method, the samples were conditioned "in situ" in the experimental device (see Sect. 2.2).

### Experimental and theoretical thermochemical methods

Vapour pressures over the liquid 2-chloro-anisole, 3-chloro-anisole, 4-chloro-anisole, 2,3-*di*-chloro-anisole, 2,4-*di*-chloro-anisole, 2,6-*di*-chloro-anisole, 3,5-*di*-chloro-anisole, 4-iodo-anisole and the solid 3,5-*di*-chloro-anisole were measured by the *transpiration method* using the nitrogen stream. They were used to obtain the standard molar enthalpies of vaporisation/sublimation, $\Delta^{g}_{l,cr}H^{o}_{m}$. The necessary details on this method have already been published elsewhere [13]. Essential for this study is that before starting the vapour pressure measurements, the sample was first pre-conditioned in the saturator at 300–320 K (within about one hour) in order to remove possible traces of volatile compounds and water. In order to assure the competition of pre-conditioning at the selected temperature, three samples were taken during the sample flashing at a certain temperature and analyzed by the GC. A constant vapour pressure at this temperature indicated that the transpiration experiments could begin. GC analysis of the transported material did not reveal any additional contamination. The absence of impurities and decomposition products was re-checked by GC analysis of the saturator content at the end of the entire series of experiments. In this work we used both the transpiration set-up constructed in Rostock [13] and the twin set-up replicated in Kazan [14]. The structural differences are small and not significant for the measuring method. Vaporisation and sublimation enthalpies, $\Delta^{g}_{l,cr}H^{o}_{m}$, were derived from the temperature dependences of the experimental vapour pressures.

An independent method to obtain the $\Delta^{g}_{l,cr}H^{o}_{m}$–values is based on the high-precision solution calorimetry [6]. We used the TAM III solution calorimeter (*TA-Instruments,* USA) to measure the solution enthalpies of halogenated anisoles in benzene. A detailed description of the calorimetric experiment has been published in previous works [15, 16]. The methodology for calculating of $\Delta^{g}_{l,cr}H^{o}_{m}$ from calorimetric results can be found elsewhere [5, 6, 17]. All experimental enthalpies of solution of halogenated anisoles in benzene are listed in Table S2.

The enthalpies and temperatures of fusion of 4-iodo-anisole and 2,3-*di*-chloro-anisole were measured by using the differential scanning calorimeter (DSC) 204 F1 Phoenix (*Netzsch,* Germany) as it was described in details previously [18]. DSC was calibrated with standard compounds (Hg, In, Sn, Bi, Zn, and CsCl). The experimental results of the DSC measurements are given in Table S3.

The quantum-chemical composite methods G3MP2 [19] and G4 [20] from the Gaussian 16 software [21] were used for calculations of $H_{298}$-values of the most stable conformers of halogenated anisoles, which were converted to the standard molar enthalpies of formation in the gas phase and discussed.

## Results and discussion

### Absolute vapour pressures measured by the transpiration method

The halogenated anisoles are volatile compounds whose vapour pressures can be readily measured by various conventional methods. However, the available absolute vapour pressures are rare and limited to the few compilations [22–24] where the methods and sample purities are unavailable, making these data of questionable quality. Our new results, measured by the transpiration method, are summarized in Table 1.

The absolute vapour pressures given in Table 1 were approximated by the following equation [13]:

$$R \times \ln(p_{\mathrm{i}}/p_{\mathrm{ref}}) = a + \frac{b}{T} + \Delta_{\mathrm{cr,l}}^{\mathrm{g}} C_{\mathrm{p,m}}^{\mathrm{o}} \times \ln\left(\frac{T}{T_0}\right), \quad (1)$$

where $\Delta_{\mathrm{cr,l}}^{\mathrm{g}} C_{\mathrm{p,m}}^{\mathrm{o}}$ (see Table S4) is the difference of the molar heat capacities of the gas and the crystal (or liquid) phases respectively [27, 28], *a* and *b* are adjustable parameters (see Table 1), $R = 8.31446\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ is the molar gas constant, and the reference pressure $p_{\mathrm{ref}} = 1$ Pa. The arbitrary temperature $T_0$ given in Eq. (1) was chosen to be $T_0 = 298.15$ K.

The available in the literature data on vapour pressures for 2-chloro-anisole (Fig. S1), 3-chloro-anisole (Fig. S2), 4-chloro-anisole (Fig. S3), 4-bromo-anisole (Fig. S4) and 4-iodo-anisole (Fig. S5) are in fair agreement with our new results. However, in most cases a correct comparison is difficult, since vapour pressures for significantly higher temperatures are given in the literature [22–24, 29]. The experimental boiling temperatures at different pressures for the halogenated anisoles have been compiled in Table S2, and as shown in Figures S1 to S4 they are in good agreement with other available data. To get more confidence in the results, we deliberately repeated the transpiration experiments for two compounds. For 2,3-*di*-chloro-anisole, the mass of the sample collected at each temperature was determined chromatographically (using the external standard) by injection into two GCs. The first device was equipped with the long capillary column (DB-1, 50 m) and the second device with the short capillary column (DB-1, 10 m). As can be seen from Fig. S6, the derived vapour pressures for this compound are practically indistinguishable. For 2,6-*di*-chloro-anisole, the transpiration experiments were carried out independently in Rostock and Kazan. As can be seen from Fig. S7, the derived vapour pressures for this compound are in good agreement.

### Vaporisation/sublimation thermodynamics of halogenated anisoles

The temperature dependencies of the vapour pressure measured with the transpiration and those available in the literature were used to derive the vaporisation/sublimation enthalpies of halogenated anisoles. One of the advantages of the transpiration method is that the vapour pressure measurements could be made at temperatures possibly close to the reference temperature $T = 298.15$ K. Therefore, the final vaporisation/sublimation enthalpies at this temperature are minimally affected by the temperature adjustment (see Sect. 3.1). The $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values derived from vapour pressures measured in this work are given in Table 1. They are compared in Table 2 with results derived from other methods.

As a consequence of the good agreement in the vapour pressures shown for each compound in Figs. S1 to S7, the vaporisation enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), indirectly derived from these data also agree very well (see Table 2). The latter values are also in good agreement with the direct calorimetric determinations made using "vacuum-sublimation" drop micro-calorimetry for fluoro- [30], chloro- [32], bromo- [33], and iodo- [34] *mono*-substituted anisoles (see Table 2). Also, our new transpiration results are in good agreement with the direct calorimetric results for *di*-chloro-substituted anisoles (see Table 2). Such a good agreement achieved for the indirect and direct values of $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) prompted to test the applicability of the newly developed solution calorimetry-based method [6, 36] for the indirect determination of the vaporisation/sublimation enthalpies of halogenated anisoles.

### Solution calorimetry to validate vaporisation/sublimation enthalpies of halogenated anisoles

As a rule, the indirectly or directly measured experimental vaporisation/sublimation enthalpies are related to the certain temperature, which in most cases deviates from the reference temperature $T = 298.15$ K. Various methods for performing the

**Table 1** Results of transpiration method for anisole derivatives: absolute vapor pressures *p*, standard molar vaporisation/sublimation enthalpies and standard molar vaporisation/sublimation entropies

| $T$/K[a] | $m$/mg[b] | $V(N_2)$[c]/dm$^3$ | $T_a$/K[d] | Flow/dm$^3$ h$^{-1}$ | $p$/Pa[e] | $u(p)$/Pa[f] | $\Delta_{l,cr}^{g}H_m^o(T)$[g]/ kJ mol$^{-1}$ | $\Delta_{l,cr}^{g}S_m^o(T)$[h]/ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 2-chloro-anisole (l): $\Delta_l^g H_m^o$(298.15 K) = (56.0 ± 0.5) kJ mol$^{-1}$ | | | | | | | | |
| $\ln(p/p_{ref}) = \frac{284.0}{R} - \frac{75523.6}{RT} - \frac{65.6}{R}\ln\frac{T}{298.15}$; $p_{ref}$ = 1 Pa | | | | | | | | |
| 288.3 | 2.81 | 2.677 | 295.2 | 5.54 | 18.34 | 0.48 | 56.6 | 124.9 |
| 289.3 | 4.40 | 3.913 | 295.2 | 3.91 | 19.61 | 0.52 | 56.5 | 124.5 |
| 291.2 | 3.61 | 2.643 | 295.2 | 5.29 | 23.74 | 0.62 | 56.4 | 124.4 |
| 292.2 | 4.40 | 2.975 | 295.2 | 5.95 | 25.72 | 0.67 | 56.4 | 124.2 |
| 295.2 | 4.60 | 2.525 | 295.2 | 5.23 | 31.63 | 0.82 | 56.2 | 123.3 |
| 297.1 | 4.33 | 2.046 | 295.2 | 4.09 | 36.68 | 0.94 | 56.0 | 122.9 |
| 298.2 | 4.27 | 1.835 | 295.2 | 5.80 | 40.31 | 1.03 | 56.0 | 122.7 |
| 301.2 | 4.84 | 1.645 | 295.2 | 5.81 | 50.88 | 1.30 | 55.8 | 122.1 |
| 304.1 | 5.05 | 1.371 | 295.2 | 5.14 | 63.59 | 1.61 | 55.6 | 121.6 |
| 306.9 | 4.85 | 1.096 | 295.2 | 4.11 | 76.29 | 1.93 | 55.4 | 120.8 |
| 307.0 | 5.34 | 1.243 | 295.2 | 4.66 | 74.12 | 1.88 | 55.4 | 120.5 |
| 310.0 | 6.14 | 1.145 | 295.2 | 4.74 | 92.43 | 2.34 | 55.2 | 120.0 |
| 312.9 | 5.22 | 0.817 | 295.2 | 2.58 | 110.12 | 2.78 | 55.0 | 119.2 |
| 313.9 | 4.71 | 0.667 | 295.2 | 1.82 | 121.63 | 3.07 | 54.9 | 119.2 |
| 315.9 | 6.47 | 0.814 | 295.2 | 3.26 | 136.98 | 3.45 | 54.8 | 118.7 |
| 318.8 | 4.78 | 0.496 | 295.2 | 1.75 | 165.88 | 4.17 | 54.6 | 118.1 |
| 318.9 | 8.10 | 0.810 | 295.2 | 3.24 | 172.02 | 4.33 | 54.6 | 118.3 |
| 321.9 | 9.54 | 0.806 | 295.2 | 3.22 | 203.58 | 5.11 | 54.4 | 117.5 |
| 324.8 | 11.06 | 0.782 | 295.2 | 3.23 | 243.31 | 6.11 | 54.2 | 116.9 |
| 327.9 | 10.48 | 0.617 | 295.2 | 2.47 | 291.91 | 7.32 | 54.0 | 116.2 |
| 330.8 | 12.44 | 0.596 | 295.2 | 2.47 | 358.16 | 8.98 | 53.8 | 115.9 |
| 333.8 | 15.70 | 0.621 | 295.2 | 2.48 | 433.68 | 10.87 | 53.6 | 115.5 |
| 336.8 | 19.87 | 0.659 | 295.2 | 2.64 | 516.40 | 12.94 | 53.4 | 114.9 |
| 339.8 | 23.61 | 0.664 | 295.2 | 2.66 | 608.33 | 15.23 | 53.2 | 114.3 |
| 3-chloro-anisole (l): $\Delta_l^g H_m^o$(298.15 K) = (54.2 ± 0.5) kJ·mol$^{-1}$ | | | | | | | | |
| $\ln(p/p_{ref}) = \frac{282.8}{R} - \frac{73756.9}{RT} - \frac{65.6}{R}\ln\frac{T}{298.15}$; $p_{ref}$ = 1 Pa | | | | | | | | |
| 278.5 | 2.48 | 3.000 | 295.2 | 4.29 | 14.70 | 0.39 | 55.5 | 125.9 |
| 280.5 | 8.64 | 8.558 | 295.9 | 6.50 | 17.91 | 0.47 | 55.4 | 125.7 |
| 281.4 | 4.33 | 4.023 | 295.2 | 4.24 | 19.00 | 0.50 | 55.3 | 125.3 |
| 283.4 | 5.89 | 4.620 | 295.9 | 6.30 | 22.51 | 0.59 | 55.2 | 124.9 |
| 284.4 | 3.70 | 2.627 | 295.2 | 4.26 | 24.76 | 0.64 | 55.1 | 124.7 |
| 286.3 | 6.01 | 3.780 | 295.9 | 6.30 | 27.94 | 0.72 | 55.0 | 124.0 |
| 287.3 | 3.88 | 2.195 | 295.2 | 4.39 | 30.95 | 0.80 | 54.9 | 124.0 |
| 289.2 | 6.84 | 3.465 | 295.9 | 6.30 | 34.55 | 0.89 | 54.8 | 123.2 |
| 290.3 | 4.48 | 2.007 | 295.2 | 4.46 | 38.86 | 1.00 | 54.7 | 123.2 |
| 292.2 | 8.80 | 3.358 | 295.9 | 6.50 | 45.71 | 1.17 | 54.6 | 122.9 |
| 293.2 | 4.25 | 1.558 | 295.2 | 4.45 | 47.46 | 1.21 | 54.5 | 122.4 |
| 295.1 | 7.73 | 2.383 | 295.9 | 6.50 | 56.45 | 1.44 | 54.4 | 122.2 |
| 296.1 | 4.82 | 1.429 | 295.2 | 3.43 | 58.57 | 1.49 | 54.3 | 121.7 |
| 296.2 | 5.00 | 1.437 | 295.2 | 4.31 | 60.38 | 1.53 | 54.3 | 121.8 |
| 298.1 | 8.57 | 2.068 | 295.9 | 6.53 | 71.91 | 1.82 | 54.2 | 121.7 |
| 299.2 | 5.34 | 1.216 | 295.2 | 3.17 | 76.06 | 1.93 | 54.1 | 121.2 |
| 301.0 | 10.11 | 1.968 | 295.9 | 6.56 | 89.06 | 2.25 | 54.0 | 121.1 |
| 302.0 | 6.65 | 1.267 | 295.2 | 3.17 | 90.71 | 2.29 | 53.9 | 120.4 |
| 304.0 | 7.98 | 1.267 | 295.9 | 3.80 | 109.06 | 2.75 | 53.8 | 120.3 |
| 305.0 | 7.15 | 1.057 | 295.2 | 3.17 | 116.74 | 2.94 | 53.8 | 120.1 |
| 306.9 | 8.30 | 1.077 | 295.9 | 3.80 | 133.27 | 3.36 | 53.6 | 119.7 |

**Table 1** (continued)

| $T$/K[a] | $m$/mg[b] | $V(N_2)$[c]/dm$^3$ | $T_a$/K[d] | Flow/dm$^3$ h$^{-1}$ | $p$/Pa[e] | $u(p)$/Pa[f] | $\Delta^g_{l,cr}H^o_m(T)$[g]/ kJ mol$^{-1}$ | $\Delta^g_{l,cr}S^o_m(T)$[h]/ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 308.0 | 5.18 | 0.645 | 295.2 | 1.94 | 138.57 | 3.49 | 53.6 | 119.2 |
| 309.9 | 6.52 | 0.710 | 295.9 | 1.51 | 158.65 | 3.99 | 53.4 | 118.8 |
| 310.9 | 6.03 | 0.598 | 295.2 | 1.99 | 173.67 | 4.37 | 53.4 | 118.8 |
| 312.9 | 8.18 | 0.705 | 295.9 | 1.51 | 200.45 | 5.04 | 53.2 | 118.5 |
| 313.9 | 7.29 | 0.613 | 295.2 | 1.94 | 204.89 | 5.15 | 53.2 | 117.9 |
| 315.8 | 7.82 | 0.579 | 295.9 | 1.51 | 232.98 | 5.85 | 53.0 | 117.6 |
| 316.9 | 8.11 | 0.548 | 295.2 | 1.93 | 254.86 | 6.40 | 53.0 | 117.5 |
| 318.8 | 9.71 | 0.587 | 295.9 | 1.60 | 285.36 | 7.16 | 52.8 | 117.1 |
| 321.8 | 8.65 | 0.428 | 295.9 | 1.51 | 348.23 | 8.73 | 52.7 | 116.6 |
| 4-chloro-anisole (l): $\Delta^g_l H^o_m(298.15\ \text{K}) = (54.1 \pm 0.3)\ \text{kJ·mol}^{-1}$ | | | | | | | | |
| $\ln(p/p_{\text{ref}}) = \frac{281.1}{\text{R}} - \frac{73689.9}{\text{RT}} - \frac{65.6}{\text{R}}\ln\frac{T}{298.15}$; $p_{\text{ref}} = 1$ Pa | | | | | | | | |
| 283.4 | 2.76 | 2.550 | 291.7 | 6.00 | 18.87 | 0.50 | 55.1 | 123.2 |
| 286.4 | 2.83 | 2.041 | 291.7 | 6.12 | 24.02 | 0.63 | 54.9 | 122.4 |
| 288.3 | 5.12 | 3.167 | 291.7 | 5.11 | 27.96 | 0.72 | 54.8 | 122.0 |
| 291.2 | 3.08 | 1.478 | 291.7 | 5.22 | 35.85 | 0.92 | 54.6 | 121.5 |
| 293.2 | 3.21 | 1.346 | 291.7 | 5.05 | 41.04 | 1.05 | 54.5 | 120.9 |
| 295.2 | 4.00 | 1.455 | 291.7 | 4.72 | 47.21 | 1.21 | 54.3 | 120.4 |
| 297.2 | 3.95 | 1.242 | 290.7 | 4.66 | 54.37 | 1.38 | 54.2 | 119.9 |
| 299.2 | 3.40 | 0.923 | 291.7 | 3.69 | 63.10 | 1.60 | 54.1 | 119.5 |
| 301.1 | 3.84 | 0.920 | 292.7 | 3.68 | 71.70 | 1.82 | 53.9 | 119.0 |
| 305.0 | 5.67 | 1.037 | 292.7 | 3.89 | 93.74 | 2.37 | 53.7 | 118.1 |
| 308.0 | 6.45 | 0.942 | 291.7 | 3.77 | 116.91 | 2.95 | 53.5 | 117.6 |
| 310.8 | 8.23 | 0.995 | 291.7 | 3.73 | 141.01 | 3.55 | 53.3 | 117.0 |
| 314.0 | 9.71 | 0.933 | 291.7 | 3.73 | 177.22 | 4.46 | 53.1 | 116.4 |
| 316.9 | 8.44 | 0.698 | 291.7 | 2.79 | 205.65 | 5.17 | 52.9 | 115.5 |
| 316.9 | 7.00 | 0.559 | 291.7 | 2.79 | 213.20 | 5.35 | 52.9 | 115.8 |
| 318.1 | 21.63 | 1.608 | 290.7 | 6.31 | 227.94 | 5.72 | 52.8 | 115.5 |
| 319.9 | 10.46 | 0.695 | 291.7 | 2.78 | 255.71 | 6.42 | 52.7 | 115.2 |
| 322.9 | 22.41 | 1.249 | 291.7 | 1.47 | 304.83 | 7.65 | 52.5 | 114.5 |
| 325.9 | 8.01 | 0.367 | 291.7 | 1.47 | 369.81 | 9.27 | 52.3 | 114.0 |
| 327.8 | 37.86 | 1.528 | 290.7 | 6.11 | 418.70 | 10.49 | 52.2 | 113.7 |
| 328.9 | 9.42 | 0.366 | 291.7 | 1.46 | 436.46 | 10.94 | 52.1 | 113.3 |
| 331.8 | 12.20 | 0.391 | 291.7 | 1.62 | 528.75 | 13.24 | 51.9 | 112.9 |
| 334.8 | 12.91 | 0.352 | 291.7 | 1.46 | 620.25 | 15.53 | 51.7 | 112.3 |
| 337.8 | 16.83 | 0.390 | 291.7 | 1.42 | 729.24 | 18.26 | 51.5 | 111.7 |
| 340.8 | 15.63 | 0.314 | 291.7 | 1.30 | 841.03 | 21.05 | 51.3 | 110.9 |
| 343.8 | 18.85 | 0.322 | 291.7 | 1.29 | 988.05 | 24.73 | 51.1 | 110.4 |
| 346.8 | 20.65 | 0.302 | 291.7 | 1.30 | 1149.55 | 28.76 | 50.9 | 109.8 |
| 2,3-*di*-chloro-anisole (l) (DB-1, 50 m)[i]: $\Delta^g_l H^o_m(298.15\ \text{K}) = (64.9 \pm 0.5)\ \text{kJ·mol}^{-1}$ | | | | | | | | |
| $\ln(p/p_{\text{ref}}) = \frac{302.0}{\text{R}} - \frac{86296.7}{\text{RT}} - \frac{71.9}{\text{R}}\ln\frac{T}{298.15}$; $p_{\text{ref}} = 1$ Pa | | | | | | | | |
| 308.5 | 2.40 | 3.080 | 294.6 | 3.080 | 10.80 | 0.30 | 64.1 | 131.9 |
| 313.5 | 2.13 | 1.834 | 293.3 | 3.144 | 16.04 | 0.43 | 63.8 | 130.8 |
| 318.4 | 2.24 | 1.334 | 294.2 | 3.202 | 23.25 | 0.61 | 63.4 | 129.5 |
| 323.5 | 2.16 | 0.881 | 293.9 | 3.202 | 33.81 | 0.87 | 63.0 | 128.4 |
| 328.5 | 2.78 | 0.786 | 294.9 | 3.144 | 48.98 | 1.25 | 62.7 | 127.5 |
| 333.4 | 2.59 | 0.514 | 294.6 | 0.881 | 69.79 | 1.77 | 62.3 | 126.5 |
| 333.5 | 2.72 | 0.541 | 296.3 | 0.928 | 69.78 | 1.77 | 62.3 | 126.4 |
| 338.4 | 2.21 | 0.325 | 295.7 | 0.928 | 94.38 | 2.38 | 62.0 | 125.2 |
| 343.4 | 2.08 | 0.220 | 296.0 | 0.881 | 131.18 | 3.30 | 61.6 | 124.2 |

**Table 1** (continued)

| $T$/K[a] | $m$/mg[b] | $V(N_2)$[c]/dm$^3$ | $T_a$/K[d] | Flow/dm$^3$ h$^{-1}$ | $p$/Pa[e] | $u(p)$/Pa[f] | $\Delta_{l,cr}^{g}H_m^o(T)$[g]/ kJ mol$^{-1}$ | $\Delta_{l,cr}^{g}S_m^o(T)$[h]/ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 348.4 | 2.95 | 0.232 | 295.8 | 0.928 | 176.30 | 4.43 | 61.2 | 123.1 |
| 353.4 | 3.04 | 0.176 | 296.5 | 0.881 | 239.42 | 6.01 | 60.9 | 122.1 |
| 2,3-*di*-chloro-anisole (l) (DB-1, 10 m)[j]: $\Delta_l^g H_m^o$(298.15 K) = (64.8 ± 0.5) kJ·mol$^{-1}$ | | | | | | | | |
| $\ln(p/p_{ref}) = \frac{302.5}{R} - \frac{86369.3}{RT} - \frac{71.9}{R}\ln\frac{T}{298.15}$; $p_{ref}$ = 1 Pa | | | | | | | | |
| 308.5 | 2.55 | 3.127 | 292.4 | 2.98 | 11.20 | 0.31 | 64.2 | 132.5 |
| 313.4 | 2.27 | 1.886 | 293.1 | 2.98 | 16.60 | 0.44 | 63.8 | 131.3 |
| 313.6 | 0.96 | 0.780 | 294.2 | 3.12 | 16.95 | 0.45 | 63.8 | 131.3 |
| 318.5 | 2.45 | 1.390 | 294.9 | 2.98 | 24.41 | 0.64 | 63.5 | 130.1 |
| 323.6 | 1.92 | 0.754 | 294.4 | 3.12 | 35.27 | 0.91 | 63.1 | 128.9 |
| 328.4 | 2.73 | 0.745 | 295.7 | 2.98 | 50.87 | 1.30 | 62.8 | 128.0 |
| 333.5 | 2.33 | 0.456 | 296.0 | 1.10 | 71.00 | 1.80 | 62.4 | 126.8 |
| 338.4 | 2.44 | 0.347 | 296.7 | 1.10 | 97.82 | 2.47 | 62.0 | 125.7 |
| 343.5 | 2.68 | 0.274 | 296.7 | 1.10 | 136.30 | 3.43 | 61.7 | 124.7 |
| 348.4 | 2.77 | 0.207 | 295.4 | 0.89 | 185.22 | 4.66 | 61.3 | 123.7 |
| 353.4 | 3.22 | 0.178 | 296.3 | 0.89 | 251.64 | 6.32 | 61.0 | 122.8 |
| 2,4-*di*-chloro-anisole (l): $\Delta_l^g H_m^o$(298.15 K) = (62.0 ± 0.5) kJ·mol$^{-1}$ | | | | | | | | |
| $\ln(p/p_{ref}) = \frac{295.9}{R} - \frac{83425.0}{RT} - \frac{71.9}{R}\ln\frac{T}{298.15}$; $p_{ref}$ = 1 Pa | | | | | | | | |
| 304.0 | 2.64 | 3.273 | 295.2 | 5.46 | 11.20 | 0.30 | 61.6 | 126.9 |
| 307.0 | 3.00 | 2.933 | 295.2 | 5.33 | 14.19 | 0.38 | 61.4 | 126.2 |
| 310.0 | 3.54 | 2.735 | 295.2 | 5.29 | 17.94 | 0.47 | 61.1 | 125.5 |
| 312.9 | 4.36 | 2.707 | 295.2 | 5.24 | 22.36 | 0.58 | 60.9 | 124.9 |
| 315.9 | 3.13 | 1.594 | 295.2 | 5.63 | 27.27 | 0.71 | 60.7 | 124.0 |
| 318.9 | 2.72 | 1.091 | 295.2 | 1.36 | 34.63 | 0.89 | 60.5 | 123.5 |
| 321.9 | 6.08 | 2.028 | 295.2 | 5.07 | 41.59 | 1.06 | 60.3 | 122.6 |
| 324.9 | 10.04 | 2.685 | 295.2 | 5.04 | 51.83 | 1.32 | 60.1 | 122.0 |
| 327.8 | 7.95 | 1.739 | 295.2 | 5.22 | 63.36 | 1.61 | 59.9 | 121.4 |
| 330.8 | 10.25 | 1.821 | 295.2 | 4.97 | 78.02 | 1.98 | 59.6 | 120.8 |
| 333.8 | 11.40 | 1.667 | 295.2 | 5.00 | 94.72 | 2.39 | 59.4 | 120.2 |
| 336.8 | 6.83 | 0.836 | 295.2 | 2.51 | 113.05 | 2.85 | 59.2 | 119.4 |
| 339.8 | 7.95 | 0.797 | 295.2 | 2.39 | 138.18 | 3.48 | 59.0 | 118.9 |
| 342.8 | 9.31 | 0.795 | 295.2 | 2.38 | 162.21 | 4.08 | 58.8 | 118.1 |
| 345.8 | 9.54 | 0.674 | 295.2 | 2.38 | 195.80 | 4.92 | 58.6 | 117.5 |
| 348.8 | 10.32 | 0.596 | 295.2 | 2.38 | 239.41 | 6.01 | 58.3 | 117.1 |
| 351.8 | 11.89 | 0.579 | 295.2 | 2.38 | 284.05 | 7.13 | 58.1 | 116.5 |
| 2,6-*di*-chloro-anisole (l) (Rostock)[k]: $\Delta_l^g H_m^o$(298.15 K) = (54.9 ± 0.3) kJ·mol$^{-1}$ | | | | | | | | |
| $\ln(p/p_{ref}) = \frac{283.8}{R} - \frac{76380.2}{RT} - \frac{71.9}{R}\ln\frac{T}{298.15}$; $p_{ref}$ = 1 Pa | | | | | | | | |
| 288.4 | 2.85 | 3.100 | 295.2 | 6.00 | 12.95 | 0.35 | 55.6 | 118.6 |
| 291.3 | 3.49 | 2.974 | 295.2 | 6.15 | 16.44 | 0.44 | 55.4 | 117.9 |
| 294.2 | 4.42 | 3.051 | 295.2 | 6.10 | 20.26 | 0.53 | 55.2 | 117.1 |
| 297.1 | 4.46 | 2.447 | 295.2 | 5.87 | 25.44 | 0.66 | 55.0 | 116.4 |
| 300.1 | 5.22 | 2.274 | 295.2 | 5.93 | 32.02 | 0.83 | 54.8 | 115.8 |
| 303.1 | 5.62 | 1.983 | 295.2 | 5.95 | 39.49 | 1.01 | 54.6 | 115.0 |
| 306.0 | 5.66 | 1.600 | 295.2 | 6.00 | 49.24 | 1.26 | 54.4 | 114.4 |
| 309.0 | 6.51 | 1.500 | 295.2 | 6.00 | 60.33 | 1.53 | 54.2 | 113.7 |
| 311.9 | 7.72 | 1.485 | 295.2 | 5.94 | 72.22 | 1.83 | 54.0 | 112.9 |
| 314.9 | 9.29 | 1.471 | 295.2 | 5.88 | 87.69 | 2.22 | 53.7 | 112.2 |
| 317.9 | 9.03 | 1.169 | 295.2 | 4.68 | 107.23 | 2.71 | 53.5 | 111.5 |
| 320.9 | 10.78 | 1.154 | 295.2 | 4.62 | 129.53 | 3.26 | 53.3 | 110.9 |
| 323.9 | 12.86 | 1.125 | 295.2 | 4.50 | 158.39 | 3.98 | 53.1 | 110.3 |

**Table 1** (continued)

| $T$/K[a] | $m$/mg[b] | $V(N_2)$[c]/dm$^3$ | $T_a$/K[d] | Flow/dm$^3$ h$^{-1}$ | $p$/Pa[e] | $u(p)$/Pa[f] | $\Delta_{l,cr}^{g}H_{m}^{o}(T)$[g]/ kJ mol$^{-1}$ | $\Delta_{l,cr}^{g}S_{m}^{o}(T)$[h]/ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 326.9 | 14.84 | 1.111 | 295.2 | 4.44 | 184.97 | 4.65 | 52.9 | 109.5 |
| 329.8 | 18.36 | 1.125 | 295.2 | 4.50 | 225.86 | 5.67 | 52.7 | 109.0 |
| 332.8 | 21.13 | 1.125 | 295.2 | 4.50 | 259.90 | 6.52 | 52.5 | 108.1 |
| 335.8 | 26.40 | 1.161 | 295.2 | 4.65 | 314.31 | 7.88 | 52.2 | 107.7 |
| 2,6-*di*-chloro-anisole (l)(Kazan)[l]: $\Delta_{l}^{g}H_{m}^{o}$(298.15 K) = (53.9 ± 0.9) kJ·mol$^{-1}$ | | | | | | | | |
| $\ln(p/p_{\mathrm{ref}}) = \frac{280.6}{R} - \frac{75381.0}{RT} - \frac{71.9}{R}\ln\frac{T}{298.15}$; $p_{\mathrm{ref}} = 1$ Pa | | | | | | | | |
| 308.1 | 16.39 | 4.091 | 300.2 | 2.73 | 57.15 | 1.45 | 53.2 | 110.7 |
| 313.1 | 14.86 | 2.727 | 300.2 | 2.73 | 77.46 | 1.96 | 52.9 | 109.3 |
| 318.2 | 14.26 | 1.863 | 300.2 | 2.73 | 108.50 | 2.74 | 52.5 | 108.3 |
| 323.2 | 13.32 | 1.281 | 300.2 | 4.05 | 147.11 | 3.70 | 52.1 | 107.1 |
| 328.0 | 13.86 | 1.011 | 300.2 | 4.05 | 193.53 | 4.86 | 51.8 | 106.0 |
| 333.2 | 14.01 | 0.742 | 300.2 | 4.05 | 266.37 | 6.68 | 51.4 | 105.1 |
| 338.2 | 15.16 | 0.617 | 300.2 | 2.06 | 345.84 | 8.67 | 51.1 | 103.9 |
| 3,5-*di*-chloro-anisole (l): $\Delta_{l}^{g}H_{m}^{o}$(298.15 K) = (60.0 ± 0.5) kJ·mol$^{-1}$ | | | | | | | | |
| $\ln(p/p_{\mathrm{ref}}) = \frac{294.4}{R} - \frac{81400.6}{RT} - \frac{71.9}{R}\ln\frac{T}{298.15}$; $p_{\mathrm{ref}} = 1$ Pa | | | | | | | | |
| 319.9 | 13.25 | 2.813 | 295.2 | 5.63 | 65.35 | 1.66 | 58.4 | 121.6 |
| 320.9 | 4.64 | 0.902 | 295.2 | 2.71 | 71.26 | 1.81 | 58.3 | 121.6 |
| 323.9 | 6.63 | 1.064 | 295.2 | 2.72 | 86.34 | 2.18 | 58.1 | 120.8 |
| 326.8 | 7.03 | 0.913 | 295.2 | 2.74 | 106.75 | 2.69 | 57.9 | 120.3 |
| 329.8 | 8.11 | 0.882 | 295.2 | 2.71 | 127.35 | 3.21 | 57.7 | 119.5 |
| 332.8 | 8.91 | 0.806 | 295.2 | 2.77 | 153.00 | 3.85 | 57.5 | 118.8 |
| 335.8 | 7.73 | 0.576 | 295.2 | 2.09 | 185.94 | 4.67 | 57.3 | 118.3 |
| 336.8 | 9.29 | 0.648 | 295.2 | 2.29 | 198.45 | 4.99 | 57.2 | 118.1 |
| 339.8 | 6.84 | 0.401 | 295.2 | 1.20 | 235.67 | 5.92 | 57.0 | 117.4 |
| 339.8 | 7.36 | 0.425 | 295.2 | 1.42 | 239.23 | 6.01 | 57.0 | 117.5 |
| 342.8 | 8.46 | 0.414 | 295.2 | 1.24 | 282.73 | 7.09 | 56.8 | 116.8 |
| 345.8 | 9.82 | 0.401 | 295.2 | 1.20 | 338.73 | 8.49 | 56.5 | 116.2 |
| 348.7 | 11.71 | 0.417 | 295.2 | 1.47 | 388.10 | 9.73 | 56.3 | 115.4 |
| 348.8 | 11.58 | 0.399 | 295.2 | 1.20 | 400.30 | 10.03 | 56.3 | 115.6 |
| 351.8 | 10.16 | 0.300 | 295.2 | 1.20 | 467.43 | 11.71 | 56.1 | 114.9 |
| 354.7 | 13.12 | 0.339 | 295.2 | 1.02 | 533.76 | 13.37 | 55.9 | 114.1 |
| 354.8 | 11.52 | 0.290 | 295.2 | 1.20 | 547.76 | 13.72 | 55.9 | 114.3 |
| 357.8 | 13.74 | 0.299 | 295.2 | 1.19 | 634.22 | 15.88 | 55.7 | 113.6 |
| 360.8 | 15.95 | 0.286 | 295.2 | 0.86 | 768.02 | 19.23 | 55.5 | 113.3 |
| 360.8 | 16.09 | 0.293 | 295.2 | 1.17 | 754.84 | 18.90 | 55.5 | 113.1 |
| 3,5-*di*-chloro-anisole (cr): $\Delta_{cr}^{g}H_{m}^{o}$(298.15 K) = (79.5 ± 1.0) kJ·mol$^{-1}$ | | | | | | | | |
| $\ln(p/p_{\mathrm{ref}}) = \frac{314.8}{R} - \frac{88255.5}{RT} - \frac{29.2}{R}\ln\frac{T}{298.15}$; $p_{\mathrm{ref}} = 1$ Pa | | | | | | | | |
| 288.3 | 2.56 | 11.276 | 295.2 | 3.62 | 3.15 | 0.08 | 79.8 | 190.8 |
| 298.1 | 4.87 | 7.219 | 295.2 | 5.63 | 9.36 | 0.26 | 79.6 | 189.8 |
| 300.0 | 3.25 | 3.844 | 295.2 | 5.63 | 11.73 | 0.32 | 79.5 | 189.8 |
| 302.0 | 3.43 | 3.264 | 295.2 | 5.76 | 14.55 | 0.39 | 79.4 | 189.6 |
| 304.0 | 3.27 | 2.531 | 295.2 | 5.63 | 17.91 | 0.47 | 79.4 | 189.4 |
| 305.9 | 3.37 | 2.122 | 295.2 | 5.79 | 22.04 | 0.58 | 79.3 | 189.4 |
| 278.5 | 4.70 | 65.249 | 295.2 | 5.98 | 1.01 | 0.03 | 80.1 | 192.1 |
| 282.4 | 3.31 | 29.332 | 295.2 | 5.71 | 1.57 | 0.04 | 80.0 | 191.4 |
| 280.4 | 2.29 | 25.950 | 295.2 | 1.67 | 1.23 | 0.04 | 80.1 | 191.6 |
| 290.2 | 2.63 | 9.165 | 295.2 | 5.67 | 3.98 | 0.10 | 79.8 | 190.7 |
| 292.2 | 2.35 | 6.553 | 295.2 | 5.54 | 4.97 | 0.13 | 79.7 | 190.5 |
| 294.1 | 2.70 | 6.077 | 295.2 | 5.79 | 6.15 | 0.18 | 79.7 | 190.3 |

**Table 1** (continued)

| $T$/K[a] | $m$/mg[b] | $V(N_2)$[c]/dm$^3$ | $T_a$/K[d] | Flow/dm$^3$ h$^{-1}$ | $p$/Pa[e] | $u(p)$/Pa[f] | $\Delta_{l,cr}^{g}H_{m}^{o}$ $(T)$[g]/ kJ mol$^{-1}$ | $\Delta_{l,cr}^{g}S_{m}^{o}$ $(T)$[h]/ J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| 296.1 | 2.61 | 4.762 | 295.2 | 5.71 | 7.60 | 0.21 | 79.6 | 190.0 |
| 284.4 | 4.26 | 29.030 | 295.2 | 5.81 | 2.04 | 0.06 | 80.0 | 191.4 |
| 286.7 | 3.70 | 19.250 | 295.2 | 5.50 | 2.67 | 0.07 | 79.9 | 191.1 |
| 307.8 | 3.94 | 2.129 | 295.2 | 5.81 | 25.64 | 0.67 | 79.3 | 188.8 |
| 4-iodo-anisole (l): $\Delta_{l}^{g}H_{m}^{o}(298.15\ \text{K}) = (63.8 \pm 0.9)\ \text{kJ·mol}^{-1}$ | | | | | | | | |
| $\ln(p/p_{\text{ref}}) = \frac{296.2}{R} - \frac{84041.0}{RT} - \frac{67.8}{R}\ln\frac{T}{298.15}$; $p_{\text{ref}} = 1$ Pa | | | | | | | | |
| 329.9 | 11.45 | 1.953 | 300.2 | 2.02 | 62.54 | 1.59 | 61.7 | 125.6 |
| 335.7 | 14.48 | 1.631 | 300.2 | 2.01 | 94.67 | 2.39 | 61.3 | 124.7 |
| 332.7 | 11.19 | 1.540 | 299.2 | 1.96 | 77.23 | 1.96 | 61.5 | 125.3 |
| 340.8 | 18.04 | 1.457 | 300.2 | 1.99 | 131.94 | 3.32 | 60.9 | 123.7 |
| 345.8 | 17.65 | 1.060 | 300.2 | 1.99 | 177.38 | 4.46 | 60.6 | 122.6 |
| 351.0 | 16.11 | 0.695 | 300.2 | 1.99 | 246.49 | 6.19 | 60.2 | 121.7 |
| 355.9 | 15.04 | 0.497 | 300.2 | 1.99 | 321.97 | 8.07 | 59.9 | 120.6 |
| 358.4 | 16.94 | 0.497 | 300.2 | 1.99 | 362.46 | 9.09 | 59.7 | 120.0 |
| 361.0 | 20.22 | 0.497 | 300.2 | 1.99 | 432.26 | 10.83 | 59.6 | 119.8 |

[a] Saturation temperature measured with the standard uncertainty ($u(T) = 0.1$ K)

[b] Mass of transferred sample condensed at $T = 243$ K

[c] Volume of nitrogen ($u(V) = 0.005$ dm$^3$) used to transfer $m$ ($u(m) = 0.0001$ g) of the sample. Uncertainties are given as standard uncertainties

[d] $T_a$ is the temperature of the soap bubble meter used for 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] Standard 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 standard uncertainties for $T$, $V$, $p$, $m$, are standard uncertainties with 0.683 confidence level

[g] Calculated using the following equation: $\Delta_{l}^{g}H_{m}^{o}(T) = -b + \Delta_{l}^{g}C_{p,m}^{o} \times T$

Uncertainty of the vaporisation enthalpy $U(\Delta_{l}^{g}H_{m}^{o})$ is the expanded uncertainty (0.95 level of confidence) calculated according to procedure described elsewhere [25, 26].Uncertainties include uncertainties from the experimental conditions and the fitting equation, vapour pressures, and uncertainties from adjustment of vaporisation enthalpies to the reference temperature $T = 298.15$ K

[h] Calculated using the following equation: $\Delta_{l}^{g}S_{m}^{o}(T) = \Delta_{l}^{g}H_{m}^{o}/T + R \times \ln(p_i/p^o)$ with $p^o = 0.1$ MPa

[i] Measured with setup in Rostock with mass determination via the long GC column (DB-1, 50 m)

[j] Measured with setup in Rostock with mass determination via the short GC column (DB-1, 10 m)

[k] Measured with setup constructed in Rostock

[l] Measured with setup constructed in Kazan

temperature adjustment of sublimation [37] and vaporisation [38] enthalpies were discussed recently.

However, the uncertainties in the $\Delta_{l,cr}^{g}H_{m}^{o}$(298.15 K)-values due to the adjustment are always included and can only be avoided if the measurements are carried out at the reference temperature $T = 298.15$ K. This applies explicitly to the method based on solution calorimetry [6, 36], where the solution enthalpy $\Delta_{\text{soln}}H_{m}^{A_i/S}$ of a solute $A_i$ in a solvent $S$ is precisely measured at $T = 298.15$ K. The solution enthalpy is related to the vaporisation/sublimation enthalpy ($\Delta_{l,cr}^{g}H_{m}^{o}$) by the following equation:

$$\Delta_{l,cr}^{g}H_{m}^{o}(298.15\ \text{K}) = \Delta_{\text{soln}}H_{m}^{A_i/S}(298.15\ \text{K}) - \Delta_{\text{solv}}H_{m}^{A_i/S}(298.15\ \text{K}) \quad (2)$$

where ($\Delta_{\text{solv}}H_{m}^{A_i/S}$) is the solvation enthalpy of a solute $A_i$ in the same solvent. The solvation enthalpy can be calculated by different ways: from the linear dependence with molar refraction [36], multiparametric correlation [39], additive method [6], or estimated with quantum-chemistry [40]. In the present work, we used the additive method [6] for calculation of the solvation enthalpy of halogen-anisoles in benzene. The solvation enthalpies were calculated as the sum of solvation contribution of the reference compound benzene, $\Delta_{\text{solv}}H_{m}^{ArH/S}$, and the contributions corresponding to a substitution of a hydrogen atom with the interested functional group X, $\Delta_{\text{solv}}H_{m}^{X\to H/S}$ (with X = F, Cl, Br, I, and $CH_3O$). Thus, the solvation enthalpy of the studied aromatic compound in the benzene, $\Delta_{\text{solv}}H_{m}^{A_i/S}$, was calculated according to the following equation:

**Table 2** Compilation of enthalpies of vaporisation/sublimation $\Delta^{g}_{l,cr}H^{o}_{m}$ of halogenated anisoles

| Compound (CAS) | Method[a] | *T*-range/ K | $\Delta^{g}_{l,cr}H^{o}_{m}(T_{av})$/ kJ mol$^{-1}$ kJ mol$^{-1}$ | $\Delta^{g}_{l,cr}H^{o}_{m}$ (298.15 K)/ kJ mol-1 kJ mol$^{-1}$ | Ref |
|---|---|---|---|---|---|
| 2-fluoro-anisole (liq) | DC | 334.9 | 57.4 ± 0.1 | 52.2 ± 1.6[c] | [30] |
| 321-28-8 | BP | 337–435 | 47.9 ± 1.0 | 53.0 ± 1.1 | Table S5 |
| | $T_b$ | | | 51.5 ± 1.5 | Table 8 |
| | *S-P* | | | 51.5 ± 1.5 | TableS20 |
| | | | | **52.2 ± 0.7**[d] | **Average** |
| 3-fluoro-anisole (liq) | DC | 329.4 | 52.6 ± 0.1 | 48.1 ± 1.4[c] | [30] |
| 456-49-5 | $J_x$ | | | 48.0 ± 1.0 | Table 6 |
| | $\Delta^{g}_{trn}H_m$ | | | 48.5 ± 0.7 | Table 7 |
| | $T_b$ | | | 48.1 ± 1.0 | Table 9 |
| | *S-P* | | | 47.8 ± 1.5 | TableS21 |
| | | | | **48.2 ± 0.4**[d] | **Average** |
| 4-fluoro-anisole (liq) | DC | 334.9 | 54.0 ± 0.1 | 48.7 ± 1.6[c] | [30] |
| 459-60-9 | CGC | | | 46.9 ± 3.6 | [31] |
| | SC | | | 46.0 ± 2.0 | [6] |
| | BP | 368–430 | 43.0 ± 0.5 | 49.2 ± 0.7 | Table S5 |
| | $J_x$ | | | 47.8 ± 0.8 | Table 6 |
| | $\Delta^{g}_{trn}H_m$ | | | 48.2 ± 1.0 | Table 7 |
| | $T_b$ | | | 47.8 ± 1.0 | Table 9 |
| | *S-P* | | | 48.0 ± 1.5 | Table S22 |
| | | | | **48.3 ± 0.4**[d] | **Average** |
| 2-chloro-anisole (liq) | n/a | 388–475 | 49.6 ± 1.5 | 57.7 ± 1.6 | [23] |
| 766-51-8 | n/a | 388–460 | 47.7 ± 2.0 | 56.0 ± 2.1 | [24] |
| | DC | 324.1 | 58.7 ± 0.1 | 55.0 ± 1.1[c] | [32] |
| | BP | 350–472 | 49.5 ± 0.9 | 56.6 ± 1.1 | Table S5 |
| | T | 288.3–339.8 | 55.1 ± 0.4 | 56.0 ± 0.5 | Table 1 |
| | $J_x$ | | | 55.3 ± 0.5 | Table 5 |
| | $\Delta^{g}_{trn}H_m$ | | | 55.5 ± 1.0 | Table 7 |
| | $T_b$ | | | 57.5 ± 1.5 | Table 8 |
| | *S-P* | | | 58.1 ± 1.5 | Table S20 |
| | | | | **55.9 ± 0.3**[d] | **Average** |
| 3-chloro-anisole (liq) | DC | 324.1 | 57.3 ± 0.2 | 53.6 ± 1.1[c] | [32] |
| 2845-89-8 | BP | 338–467 | 47.2 ± 0.9 | 53.9 ± 1.1 | Table S5 |
| | T | 278.5–321.8 | 54.2 ± 0.4 | 54.2 ± 0.5 | Table 1 |
| | SC | | | 56.2 ± 1.1 | Table 3 |
| | $J_x$ | | | 54.4 ± 0.6 | Table 5 |
| | $\Delta^{g}_{trn}H_m$ | | | 54.1 ± 0.7 | Table 7 |
| | $T_b$ | | | 54.2 ± 1.0 | Table 9 |
| | *S-P* | | | 54.9 ± 1.5 | Table S21 |
| | | | | **54.3 ± 0.3**[d] | **Average** |
| 4-chloro-anisole (liq) | DC | 324.0 | 58.5 ± 0.2 | 54.8 ± 1.1[c] | [32] |
| 623-12-1 | BP | 345–471 | 47.8 ± 0.9 | 54.9 ± 1.1 | Table S5 |
| | T | 283.4–346.8 | 53.2 ± 0.2 | 54.1 ± 0.3 | Table 1 |
| | $J_x$ | | | 54.8 ± 0.5 | Table 5 |
| | $\Delta^{g}_{trn}H_m$ | | | 54.0 ± 0.7 | Table 7 |
| | $T_b$ | | | 54.9 ± 1.0 | Table 9 |
| | *S-P* | | | 55.4 ± 1.5 | Table S22 |
| | | | | **54.4 ± 0.2**[c] | **Average** |
| 2-bromo-anisole (liq) | DC | 329.0 | 66.2 ± 0.2 | 61.8 ± 1.3[c] | [33] |
| 578-57-4 | BP | 346–489 | 52.7 ± 1.6 | 60.0 ± 1.7 | Table S5 |
| | $T_b$ | | | 61.0 ± 1.5 | Table 8 |
| | *S-P* | | | 60.7 ± 1.5 | Table S20 |
| | | | | **61.0 ± 0.7**[d] | **Average** |

**Table 2** (continued)

| Compound (CAS) | Method[a] | $T$-range/ K | $\Delta^{g}_{l,cr}H^{o}_{m}(T_{av})$/ kJ mol$^{-1}$ kJ mol$^{-1}$ | $\Delta^{g}_{l,cr}H^{o}_{m}$ (298.15 K)/ kJ mol-1 kJ mol$^{-1}$ | Ref |
|---|---|---|---|---|---|
| 3-bromo-anisole (liq) | DC | 328.9 | 62.4 ± 0.2 | 58.0 ± 1.3[c] | [33] |
| 2398-37-0 | BP | 347–484 | 50.4 ± 0.7 | 58.1 ± 0.9 | Table S5 |
| | $J_x$ | | | 58.0 ± 1.0 | Table 6 |
| | $\Delta^{g}_{trn}H_m$ | | | 58.0 ± 1.0 | Table 7 |
| | $T_b$ | | | 57.2 ± 1.0 | Table 9 |
| | *S-P* | | | 57.7 ± 1.5 | Table S21 |
| | | | | **57.9 ± 0.4**[d] | **Average** |
| 4-bromo-anisole (liq) | n/a | 321–496 | 49.8 ± 2.0 | 57.2 ± 2.1 | [24] |
| 104-92-7 | DC | 329.0 | 62.8 ± 0.1 | 58.3 ± 1.4[c] | [33] |
| | n/a | 322–496 | 50.5 ± 1.2 | 57.1 ± 1.3 | [22] |
| | BP | 368–497 | 50.5 ± 1.2 | 59.1 ± 1.4 | Table S5 |
| | $J_x$ | | | 58.5 ± 0.8 | Table 6 |
| | $\Delta^{g}_{trn}H_m$ | | | 57.6 ± 1.0 | Table 7 |
| | $T_b$ | | | 59.3 ± 1.0 | Table 9 |
| | *S-P* | | | 58.3 ± 1.5 | Table S22 |
| | | | | **58.3 ± 0.4**[d] | **Average** |
| 2-iodo-anisole (liq) | DC | 324.2 | 69.1 ± 0.2 | 65.3 ± 1.4[c] | [34] |
| 529-28-2 | BP | 399–514 | 54.7 ± 0.3 | 65.0 ± 0.9 | Table S5 |
| | $J_x$ | | | 65.2 ± 1.0 | Table 6 |
| | $T_b$ | | | 65.3 ± 1.5 | Table 8 |
| | *S-P* | | | 65.0 ± 1.5 | Table S20 |
| | | | | **65.2 ± 0.5**[c] | **Average** |
| 3-iodo-anisole (liq) | DC | 324.2 | 66.3 ± 0.1 | 62.5 ± 1.3[c] | [34] |
| 766-85-8 | BP | 401–518 | 49.7 ± 1.0 | 60.3 ± 1.3 | Table |
| | $T_b$ | | | 63.1 ± 1.0 | Table 9 |
| | *S-P* | | | 62.3 ± 1.5 | Table S21 |
| | | | | **62.3 ± 0.6**[d] | **Average** |
| 4-iodo-anisole (liq) | IT | 401.4–479.8 | 53.5 ± 0.3 | 63.0 ± 0.8 | [29] |
| 696-62-8 | n/a | 401–520 | 52.4 ± 2.0 | 63.4 ± 2.2 | [24] |
| | T | 329.9–361.0 | 60.7 ± 0.8 | 63.8 ± 0.9 | Table 1 |
| | $J_x$ | | | 63.1 ± 1.0 | Table 6 |
| | $\Delta^{g}_{trn}H_m$ | | | 62.3 ± 1.0 | Table 7 |
| | $T_b$ | | | 61.9 ± 1.0 | Table 9 |
| | *S-P* | | | 63.1 ± 1.5 | Table S22 |
| | | | | **62.9 ± 0.4**[c] | **Average** |
| 4-iodo-anisole (cr) | DC | 349.4 | 90.4 ± 0.3 | 82.6 ± 1.5[c] | [34] |
| | K | 271.2–287.1 | 83.1 ± 1.5 | 83.0 ± 1.7 | [34] |
| | SC | | | 80.4 ± 0.6 | Table 3 |
| | $T_{fus}$ | | | 81.9 ± 0.6 | Table 4 |
| | | | | **81.4 ± 0.4**[d] | **Average** |
| 2,3-*di*-chloro-anisole (liq) | T | 308.5–353.4 | 62.6 ± 0.4 | 64.9 ± 0.5 | Table 1 |
| 1984-59-4 | T | 308.5–353.4 | 62.5 ± 0.4 | 64.8 ± 0.5 | Table 1 |
| | $J_x$ | | | 64.4 ± 0.7 | Table 5 |
| | | | | **64.8 ± 0.3**[c] | **Average** |
| 2,3-*di*-chloro-anisole (cr) | DC | 324.0 | 88.6 ± 0.3 | 83.6 ± 1.5[c] | [12] |
| | $T_{fus}$ | | | 83.6 ± 0.5 | Table 4 |
| | SC | | | 79.9 ± 1.0 | Table 3 |
| | | | | **82.9 ± 0.4**[d] | **Average** |
| 2,4-*di*-chloro-anisole (liq) | DC | 324.1 | 67.8 ± 0.1 | 62.8 ± 1.5[c] | [12] |
| 1984-58-3 | T | 304.0–351.8 | 59.9 ± 0.4 | 62.0 ± 0.5 | Table 1 |
| | SC | | | 59.9 ± 1.0 | Table 3 |
| | $J_x$ | | | 61.9 ± 0.5 | Table 5 |

**Table 2** (continued)

| Compound (CAS) | Method[a] | $T$-range/ K | $\Delta^{g}_{l,cr}H^{o}_{m}(T_{av})$/ kJ mol$^{-1}$ kJ mol$^{-1}$ | $\Delta^{g}_{l,cr}H^{o}_{m}$ (298.15 K)/ kJ mol-1 kJ mol$^{-1}$ | Ref |
|---|---|---|---|---|---|
| | | | | **61.8 ± 0.3** | **Average** |
| 2,5-*di*-chloro-anisole (liq) | $J_x$ | | | 61.4 ± 0.5 | Table 5 |
| 1984-58-3 | | | | | |
| 2,6-*di*-chloro-anisole (liq) | DC | 324.0 | 61.1 ± 0.1 | 56.1 ± 1.5[c] | [12] |
| 1984-65-2 | T | 288.4–335.8 | 54.0 ± 0.2 | 54.9 ± 0.3 | Table 1 |
| | T | 308.1–338.2 | 52.2 ± 0.8 | 53.9 ± 0.9 | Table 1 |
| | $J_x$ | | | 55.0 ± 0.7 | Table 5 |
| | | | | **54.9 ± 0.3**[d] | **Average** |
| 3,4-*di*-chloro-anisole (liq) | $J_x$ | | | 62.1 ± 0.5 | Table 5 |
| 36404-30-5 | | | | | |
| 3,5-*di*-chloro-anisole (liq) | T | 319.9–360.8 | 57.0 ± 0.4 | 60.0 ± 0.5 | Table 1 |
| 33719-74-*3* | $J_x$ | | | 60.5 ± 0.5 | Table 5 |
| | | | | **60.2 ± 0.3**[d] | **Average** |
| 3,5-*di*-chloro-anisole (cr) | DC | 323.9 | 84.0 ± 0.4 | 79.0 ± 1.6[c] | [12] |
| | T | 288.3–307.8 | 79.7 ± 0.6 | 79.5 ± 1.0 | Table 1 |
| | SC | | | 80.6 ± 1.1 | Table 3 |
| | | | | **79.8 ± 0.7**[d] | **Average** |
| 2,4,5-*tri*-chloro-anisole (liq) | $\Delta^{g}_{trn}H_{m}$ | | | 69.3 ± 1.0 | Table 7 |
| 6130-75-2 | | | | | |
| 2,4,6-*tri*-chloro-anisole (liq) | S | 319.7–368.3 | 59.4 ± 0.1 | 62.9 ± 0.3 | [35] |
| 87-40-1 | $J_x$ | | | 62.7 ± 1.0 | Table 5 |
| | $\Delta^{g}_{trn}H_{m}$ | | | 62.8 ± 1.0 | Table 7 |
| | $T_b$ | | | 62.4 ± 1.0 | Table 9 |
| | | | | **62.8 ± 0.3**[d] | **Average** |
| 2,4,6-*tri*-chloro-anisole (cr) | S | 297.1–329.8 | 83.1 ± 0.4 | 83.6 ± 0.7 | [35] |
| | $T_{fus}$ | | | 83.6 ± 0.7 | Table 4 |
| | | | | **83.6 ± 0.5**[d] | **Average** |
| 2,4,6-*tri*-bromo-anisole (liq) | S | 336.6–391.7 | 67.8 ± 0.1 | 73.1 ± 0.4 | [35] |
| 607-99-8 | $T_b$ | | | 72.4 ± 1.0 | Table 9 |
| | | | | **73.0 ± 0.4**[d] | **Average** |
| 2,4,6-*tri*-bromo-anisole (cr) | S | 330.7–356.4 | 92.0 ± 0.4 | 93.5 ± 0.9 | [35] |
| | $T_{fus}$ | | | 94.0 ± 1.2 | Table 4 |
| | | | | **93.7 ± 0.7**[d] | **Average** |
| 2,4-*di*-iodo-anisole (cr) | SC | | | 101.2 ± 1.4 | Table 3 |
| 28896-47-1 | | | | | |
| 2,4-*di*-iodo-anisole (liq) | $T_{fus}$ | | | 84.1 ± 1.8 | Table 4 |

[a] Techniques: DC = "vacuum-sublimation" drop micro-calorimetry; T = transpiration method; n/a = not available; $J_x$—from correlation of experimental vaporisation enthalpies with Kovats indices (see text); BP—from experimental boiling temperatures reported at different pressures compiled in the literature(Table S5); SC = from high-precision solution enthalpy; $T_b$ = from correlation of vaporisation enthalpies with the normal boiling points; CGC = correlation gas-chromatography; $T_{fus}$ = calculated as the difference between sublimation and fusion enthalpy; S = static method; $\Delta^{g}_{trn}H_{m}$ = from correlation of experimental vaporisation enthalpies with the solution enthalpies in chromatographic liquid phase (see text); *S-P* = from structure–property correlations (see text). K = Knudsen effusion method; IT = static method (isoteniscope)

[b] Adjusted to the reference temperature $T$ = 298.15 K according to the Kirchhoff´s Law with $\Delta^{g}_{cr,l}C^{o}_{p,m}$-values derived according to empirical equations developed by Chickos and Acree [27, 28]

[c] Uncertainties in the temperature adjustment of vaporisation enthalpies to the reference temperature $T$ = 298.15 K are estimated to account with 30% to the total adjustment for the drop-calorimetry measurements

[d] Weighted mean value (the uncertainty was taken as the weighing factor). Uncertainty of the vaporisation enthalpy is expressed as the expanded uncertainty (0.95 level of confidence, $k$ = 2). Values highlighted in bold were recommended for thermochemical calculations

$$\Delta_{\mathrm{solv}}H_{\mathrm{m}}^{\mathrm{A_i/S}}(298.15\,\mathrm{K}) = \Delta_{\mathrm{solv}}H_{\mathrm{m}}^{\mathrm{ArH/S}}(298.15\,\mathrm{K}) + n \times \Delta_{\mathrm{solv}}H_{\mathrm{m}}^{\mathrm{X\rightarrow H/S}}(298.15\,\mathrm{K}) \tag{3}$$

The solution enthalpies of halogen-anisoles directly measured in benzene are given in Table 3, column 2 (primary experimental data are collected in Table S2). The solution enthalpies of halogen-anisoles estimated by the group-additivity are given in Table 3, column 3. The resulting vaporisation/sublimation enthalpies of halogen-anisoles derived according to Eq. (2) are given in Table 3, column 4, as well as in Table 2, where they are labeled as solution calorimetry and compared with results obtained by other methods.

As can be seen in Table 2, values obtained by using Eq. (2) are in agreement (within the combined experimental uncertainties) with the directly and indirectly measured $\Delta_{\mathrm{l,cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K). This agreement can be considered as verification of the methods used in this work for temperature adjustments of vaporisation/sublimation enthalpies, as well as for the reliability of the $\Delta_{\mathrm{cr,l}}^{\mathrm{g}}C_{p,\mathrm{m}}^{\mathrm{o}}$-values (see Table S4) used in the current work for this purpose.

## Consistency of the solid–gas, liquid–gas, and solid–liquid phase-transition enthalpies

The enthalpies of sublimation, vaporisation and fusion at 298.15 K are related by the following equation:

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\,\mathrm{K}) = \Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\,\mathrm{K}) + \Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\,\mathrm{K}) \tag{4}$$

This equation can be used for validation of the enthalpies of phase transitions obtained by various methods, as well as to determine the unknown value from the other values. In the present work, the literature and measured in the work enthalpies of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}(T_{\mathrm{fus}})$ were adjusted from $T_{\mathrm{fus}}$ to 298.15 K using the empirical approach suggested by Chickos and Acree [28].The enthalpies of fusion $\Delta_{\mathrm{cr}}^{\mathrm{l}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) are given in Table 4, column 3 and used for the evaluation of internal consistency of phase transitions according to Eq. (4).

The enthalpy of fusion of 2,3-*di*-chloro-anisole measured in this work differs significantly from the DSC result from Ref. [12], however, according to Eq. (4) our value is consistent with the difference between the evaluated in Table 2 sublimation and vaporisation enthalpy for this compound. Also in the case of 3,5-*di*-chloro-anisole the fusion enthalpy estimated according to Eq. (4) and recalculated to the $T_{\mathrm{fus}}$ (see Table 4, column 3) is consistent apparently with the evaluated solid–gas and liquid gas phase transition enthalpies, but differs significantly from the experimental fusion enthalpy of 3,5-*di*-chloro-anisole determined in [12]. The reason for the discrepancy in the enthalpies of fusion for 2,3-*di*-chloro-anisole and 3,5-*di*-chloro-anisole observed in Table 4 is not clear, but the consistency of the phase transition enthalpies shown in Table 4 allows a recommendation of the results from this work for further thermochemical calculations. In addition, the vaporisation enthalpies for 2,4,6-*tri*-chloro-anisole, 2,4,6-*tri*-bromo-anisole and 2,4-*di*-iodo-anisole were derived for the first time Eq. (4) and involved in "structure–property" correlations.

## Chromatographic Kovats retention indices for validation of experimental vaporisation enthalpies

It is known that there is a linear relationship between the Kovats retention indices ($J_x$) [43] and the vaporization enthalpies at 298.15 K for compounds with similar structures or homologous series [44]:

$$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(298.15\mathrm{K}) = c + d \times J_x \tag{5}$$

To calculate the vaporisation enthalpies at 298.15 K, the literature Kovats retention indices [45–50]for halogenated anisoles were collected. It turned out that there is no comprehensive $J_x$ data set of halogen-substituted anisoles in the

**Table 3** Solution and solvation enthalpies of halogen-anisoles in benzene and vaporisation/sublimation enthalpies of halogenated anisoles derived according to Eq. (2) (at $T$=298.15 K)

| Compound | $\Delta_{\mathrm{soln}}H_{\mathrm{m}}^{\mathrm{A_i/S}}$ a/ kJ mol$^{-1}$ | $-\Delta_{\mathrm{solv}}H_{\mathrm{m}}^{\mathrm{A_i/S}}$ b/ kJ mol$^{-1}$ | $\Delta_{\mathrm{l,cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ c/ kJ mol$^{-1}$ |
|---|---|---|---|
| 3-chloroanisole (l) | 3.7 ± 0.5 | 52.5 ± 1.0 | 56.2 ± 1.1 |
| 2,3-*di*-chloroanisole (cr) | 19.3 ± 0.3 | 58.6 ± 1.0 | 79.9 ± 1.0 |
| 2,4-*di*-chloroanisole (l) | 1.3 ± 0.2 | 58.6 ± 1.0 | 59.9 ± 1.0 |
| 3,5-*di*-chloroanisole (cr) | 22.0 ± 0.5 | 58.6 ± 1.0 | 80.6 ± 1.1 |
| 4-iodo-anisol (cr) | 19.3 ± 0.3 | 61.1 ± 1.0 | 80.4 ± 1.0 |
| 2,4-*di*-iodo-anisol (cr) | 25.4 ± 1.0 | 75.8 ± 1.0 | 101.2 ± 1.4 |

[a] Measured in this work (see Table S2)

[b] Calculated according to Eq. (3) with contributions given in Table S6

[c] Calculated according to Eq. (2). Uncertainties are given as expanded uncertainties with 0.95 confidence level and k ≈ 2

**Table 4** Phase transitions thermodynamics of halogenated anisoles measured in this work and available in the literature

| Compounds | $T_{fus}$/K | $\Delta_{cr}^{l}H_m^o(T_{fus})$/kJ mol$^{-1}$ | $\Delta_{cr}^{l}H_m^o$ $^a$/kJ mol$^{-1}$ | $\Delta_{l}^{g}H_m^o$ $^b$/kJ mol$^{-1}$ 298.15 K | $\Delta_{cr}^{g}H_m^o$ $^c$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 |
| 4-iodo-anisole | 321.8 ± 0.3 | 20.0 ± 0.4$^d$ | 19.0 ± 0.5 | 62.9 ± 0.4 | 81.9 ± 0.6 |
| 2,3-*di*-chloro-anisole | 304.1 ± 0.2 | (22.0 ± 0.2) [12] | | | |
| | 304.8 ± 0.3 | 19.3 ± 0.3$^d$ | 18.8 ± 0.4 | 64.8 ± 0.3 | 83.6 ± 0.5 |
| 3,5-*di*-chloro-anisole | 310.5 ± 0.2 | (23.7 ± 0.2) [12]<br>20.0 ± 1.0$^e$ | 19.9 ± 0.7$^f$ | 60.2 ± 0.3 | 80.1 ± 0.6 |
| 2,4,6-*tri*-chloro-anisole | 332.5 ± 0.1 | 22.4 ± 0.3 [35] | 20.8 ± 0.6 | 62.8 ± 0.3 | 83.6 ± 0.7 |
| 2,4,6-*tri*-bromo-anisole | 359.4 ± 0.2 | 23.9 ± 0.6 [35] | 21.0 ± 1.1 | 73.0 ± 0.4 | 94.0 ± 1.2 |
| 2,4-*di*-iodo-anisole | 341 ± 1 [41] | 19.2 ± 1.0$^g$ | 17.1 ± 1.2 | 84.1 ± 1.8$^h$ | 101.2 ± 1.4$^i$ |

Uncertainties in this table are presented as expanded uncertainties (0.95 level of confidence with $k = 2$). Values in brackets seem to be questionable

[a] The experimental enthalpies of fusion $\Delta_{cr}^{l}H_m^o$ measured at $T_{fus}$ and adjusted to 298.15 K according to procedure developed by Chickos and Acree [28]:

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

where $\Delta_{cr}^{g}C_{p,m}^o$ and $\Delta_{l}^{g}C_{p,m}^o$ were taken from Table S4. Uncertainties in the temperature adjustment of fusion enthalpies from $T_{fus}$ to the reference temperature are estimated to account with 30% to the total adjustment [28]

[b] Evaluated values from Table 2 (see main text)

[c] Calculated as the sum of column 4 and 5 in this table

[d] Measured in the present work (see Table S3)

[e] The enthalpy of fusion $\Delta_{cr}^{l}H_m^o(298.15\text{ K}) = 19.9 \pm 0.7$ kJ mol$^{-1}$ was adjusted to $T_{fus}$ according to procedure developed by Chickos and Acree [28]

[f] Calculated as the difference between sublimation and vaporisation enthalpy evaluated in Table 2

[g] The enthalpy of fusion $\Delta_{cr}^{l}H_m^o = \text{WC} \times T_{fus}$ was calculated with help of the Walden Constant (WC) with the original value WC = 56.5 J K$^{-1}$ mol$^{-1}$ [42]

[h] Calculated as the difference between column 6 and 4 in this table

[i] Experimental value derived in this work from the solution calorimetry (see Tables 3)

literature. There are only a few sets that contain halogen-substituted anisoles instead. The available data were measured on different chromatography columns and cannot be treated together. For this reason, the correlation according to Eq. (5) was performed for each dataset (see Tables S7-S17). The evaluated $\Delta_{l}^{g}H_m^o$(298.15 K)-values using different types of columns are listed in Tables 5 and 6.

Primary data of the retention indices and fit parameters in Eq. (5) are given in Tables S7–S17 of supplementary material. As can be seen from these tables, the high correlation coefficients $R^2$ of Eq. (5) for each data set prove the reliability of the vaporisation enthalpies evaluated in Tables 5 and 6. The vaporisation enthalpies derived in Tables S7–S17 within and between different data sets agree within ± 1 kJ mol$^{-1}$.Therefore, in order to have more confidence in the $\Delta_{l}^{g}H_m^o$(298.15 K) values of halogenated anisoles, the weighted average values were calculated for each halogen-anisole, which are reported in the last columns of Tables 5 and 6, respectively. These values are labeled as $J_x$ and compared with results obtained by other methods in Table 2.

## Validation of vaporisation enthalpies using the enthalpy of transfer in gas chromatography

In the previous section it was shown how directly measured retention indices by gas chromatography can be used for evaluation of the enthalpy of vaporization at 298.15 K. This section continues the application of the gas-chromatography methods for "structure–property" correlations. The temperature dependence of chromatographic retention times provides the energetics of the interactions between the solute and the column stationary phase. The enthalpy of transfer of the solute from the chromatographic stationary phase to the gas phase, $\Delta_{trn}^{g}H_m(T)$,is related to the $\Delta_{l}^{g}H_m^o$(298.15 K)-values [51, 52]:

$$\Delta_{l}^{g}H_m^o(298.15\,\text{K}) = e + f \times \Delta_{trn}^{g}H_m(T) \tag{6}$$

The $\Delta_{trn}^{g}H_m(T)$-values for halogen-substituted anisoles in Apieson L [53] and Squalane [54] as stationary phases and fitting parameters of Eq. (6) are given in Tables S15–S19 of supplementary material. The high correlation coefficients $R^2$ of Eq. (6) for each data set demonstrate the reliability of the

**Table 5** Compilation of vaporisation enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), of chloro-substituted anisoles derived from correlations with retention indices, $J_x$, collected in Tables S7–S13 (in kJ mol$^{-1}$)

| Compound | S7 | S8 | S9 | S10 | S11 | S12 | S13 | Average[a] |
|---|---|---|---|---|---|---|---|---|
| 2-chloro-anisole | | 54.9 | 55.1 | | 56.5 | 54.7 | | 55.3 ± 0.5 |
| 3-chloro-anisole | | 54.2 | 54.6 | | | 54.4 | | 54.4 ± 0.6 |
| 4-chloro-anisole | | 54.6 | 54.3 | | 55.8 | 54.6 | 55.1 | 54.8 ± 0.5 |
| 2,3-*di*-chloro-anisole | 65.1 | | | 63.7 | | | | 64.4 ± 0.7 |
| 2,4-*di*-chloro-anisole | 62.0 | 61.7 | 61.3 | 62.4 | | | | 61.9 ± 0.5 |
| 2,5-*di*-chloro-anisole | 61.2 | 61.3 | 61.1 | 61.8 | | | | 61.4 ± 0.5 |
| 2,6-*di*-chloro-anisole | 55.2 | | | 54.9 | | | | 55.0 ± 0.7 |
| 3,4-*di*-chloro-anisole | 63.0 | 62.1 | 61.2 | 62.1 | | | | 62.1 ± 0.5 |
| 3,5-*di*-chloro-anisole | 59.4 | 60.5 | 60.9 | 61.2 | | | | 60.5 ± 0.5 |
| 2,4,6-*tri*-chloro-anisole | | | 62.7 | | | | | 62.7 ± 1.0 |

[a] Weighted mean value (the uncertainty given for each compound in Tables S7–S13 was taken as the weighing factor). Uncertainties of the vaporisation enthalpies are expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$)

**Table 6** Compilation of vaporisation enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K), of halogenated anisoles derived from correlations with retention indices collected in Tables S11–S14 (in kJ mol$^{-1}$)

| Compound | S11 | S12 | S13 [b] | S14 | Average[a] |
|---|---|---|---|---|---|
| 3-fluoro-anisole | | 48.0 | | | 48.0 ± 1.0 |
| 4-fluoro-anisole | | 48.1 | 47.1 | | 47.8 ± 0.8 |
| 3-bromo-anisole | | | | 58.0 | 58.0 ± 1.0 |
| 4-bromo-anisole | | | 58.7 | 58.4 | 58.5 ± 0.8 |
| 2-iodo-anisole | 65.2 | | | | 65.2 ± 1.0 |
| 4-iodo-anisole | | | 63.1 | | 63.1 ± 1.0 |

[a] Weighted mean value (the uncertainty given for each compound in Tables S11–S14 was taken as the weighing factor). Uncertainties of the vaporisation enthalpies are expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$)

vaporisation enthalpies evaluated according to Eq. (6). The vaporisation enthalpies derived in Tables S15–S19 within and between different data sets agree within ± 1 kJ mol$^{-1}$. Therefore, for more confidence in the $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K)-values of halogenated anisoles, the weighted average values were calculated for each halogen-anisole, which are reported in the last column of Tables 7.

These values are labeled as $\Delta_{\mathrm{trn}}^{\mathrm{g}}H_{\mathrm{m}}(T)$ and compared with results obtained by other methods in Table 2.

## Validation of vaporisation enthalpies using normal boiling temperatures $T_{\mathrm{b}}$

The linear relationship between vaporization enthalpy and boiling point ($T_{\mathrm{b}}$) can be an additional valuable tool in validating values of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$(298.15 K) for thermally stable compounds [4]. The origin of this relationship is known as Trouton´s rule [55], where the ratio of vaporization enthalpy and boiling temperature is constant. Correlations within structurally similar series of molecules increase the reliability of the determined vaporization enthalpies. The normal boiling points of halogen

**Table 7** Compilation of vaporisation enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K), of halogenated anisoles derived from correlations with solution enthalpies, $\Delta_{\mathrm{trn}}^{\mathrm{g}}H_{\mathrm{m}}(T)$, collected in Tables S15-S19 (in kJ mol$^{-1}$)

| Compound | S15 | S16 | S17 | S18 | S19 | Average[a] |
|---|---|---|---|---|---|---|
| 3-fluoro-anisole | | 48.5 | | | | 48.5 ± 1.0 |
| 4-fluoro-anisole | | 48.2 | | | | 48.2 ± 1.0 |
| 2-chloro-anisole | 55.5 | | | | | 55.5 ± 1.0 |
| 3-chloro-anisole | 54.3 | | 53.9 | | | 54.1 ± 0.7 |
| 4-chloro-anisole | 54.3 | | 53.8 | | | 54.0 ± 0.7 |
| 2,4,5-*tri*-chloro-anisole | 69.3 | | | | | 69.3 ± 1.0 |
| 2,4,6-*tri*-chloro-anisole | 62.8 | | | | | 62.8 ± 1.0 |
| 3-bromo-anisole | | | | 58.0 | | 58.0 ± 1.0 |
| 4-bromo-anisole | | | | 57.6 | | 57.6 ± 1.0 |
| 4-iodo-anisole | | | | | 62.3 | 62.3 ± 1.0 |

[a] Weighted mean value (the uncertainty given for each compound in Tables S15–S19 was taken as the weighing factor). Uncertainties of the vaporisation enthalpies are expressed as the expanded uncertainty (0.95 level of confidence, $k = 2$)

substituted anisoles were compiled from the literature [41]and used to establish a linear relationship with the experimental enthalpies of vaporisation:

$$\Delta_l^g H_m^o(298\,\mathrm{K})/\mathrm{kJ\,mol^{-1}} = -23.4 + 0.1725 \times T_b \quad \text{for 2-substituted} \left(R^2 = 0.9679\right) \tag{7}$$

$$\Delta_l^g H_m^o(298\,K)/\mathrm{kJ\,mol^{-1}} = -27.3 + 0.1746 \times T_b \quad \text{for 3-and 4-substituted} \left(R^2 = 0.9919\right) \tag{8}$$

The *ortho*-isomers (see Eq. 7) and the *meta*- and *para*-isomers (see Eq. 8) were found to split into two distinct lines. The obvious reason for such a separation is the different degree of molecular structuring in the liquid phase. According to the data evaluated in Table 2, the vaporization enthalpies of the *ortho*-isomers are systematically higher than those of the *meta*- and *para*-isomers (regardless of the halogen type). The enthalpies of vaporisation calculated using Eqs. (7) and (8) are listed in Tables 8 and 9 (last columns). As can be seen from both tables, the enthalpies of vaporization derived from boiling temperatures agree well with experimental data (we used for correlations only results obtained by drop-calorimetry, transpiration and static methods). The values of the enthalpies of vaporisation which were estimated from the $\Delta_l^g H_m^o(298.15\text{ K})$—$T_b$ correlation are labeled as $T_b$ and compared with results obtained by other methods in Table 2.

## Validation of vaporisation enthalpies using "structure–property" correlations

The "structure–property" (*S–P*) correlations are extremely useful for validating new and already available experimental data. Indeed, the thermodynamic properties of similarly shaped compounds are expected to follow a clear trend through comparison. For example, the properties of halogenated anisoles (methoxy-substituted benzenes) are expected to correlate with the

**Table 8** Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o(298.15\text{ K})$, of 2-halogen-substituted anisoles with their normal boiling temperatures ($T_b$)

| Compound | $T_b$ [a]/K | $\Delta_l^g H_m^o(298.15\text{ K})_{exp}$ [b]/kJ mol$^{-1}$ | $\Delta_l^g H_m^o(298.15\text{ K})_{calc}$ [c]/kJ mol$^{-1}$ | Δ[d]/kJ mol$^{-1}$ |
|---|---|---|---|---|
| 2-fluoro-anisole | 435 | 52.2 | 51.6 | 0.6 |
| 2-chloro-anisole | 469 | 56.0 | 57.5 | − 1.5 |
| 2-bromo-anisole | 489 | 61.8 | 61.0 | 0.8 |
| 2-iodo-anisole | 514 | 65.3 | 65.3 | 0.0 |

[a] Normal boiling temperatures [41]

[b] Experimental data from Table 2, either from drop-calorimetry or from the transpiration method. Uncertainties are twice standard deviation

[c] Calculated using Eq. (7) with the assessed expanded uncertainty of ± 1.5 kJ mol$^{-1}$

[d] Difference between column 3 and 4 in this table

**Table 9** Correlation of vaporisation enthalpies, $\Delta_l^g H_m^o$ (298.15 K), of 3-, 4- and 2,4,6-substituted anisoles with their normal boiling temperatures ($T_b$)

| Compound | $T_b$ [a]/K | $\Delta_l^g H_m^o(298\text{ K})_{exp}$ [b]/ kJ mol$^{-1}$ | $\Delta_l^g H_m^o(298\text{ K})_{calc}$ [c]/ kJ mol$^{-1}$ | Δ[d]/kJ mol$^{-1}$ |
|---|---|---|---|---|
| 3-fluoro-anisole | 432 | 48.1 | 48.1 | 0.0 |
| 4-fluoro-anisole | 430 | 48.7 | 47.8 | 0.9 |
| 3-chloro-anisole | 467 | 53.6 | 54.2 | − 0.6 |
| 4-chloro-anisole | 471 | 54.8 | 54.9 | − 0.1 |
| 3-bromo-anisole | 484 | 58.0 | 57.2 | 0.8 |
| 4-bromo-anisole | 496 | 58.3 | 59.3 | − 1.0 |
| 3-iodo-anisole | 518 | 62.5 | 63.1 | − 0.6 |
| 4-iodo-anisole | 511 | 61.8 | 61.9 | − 0.1 |
| 2,4,6-*tri*-chloro-anisole | 514 | 62.9 | 62.4 | 0.5 |
| 2,4,6-*tri*-bromo-anisole | 571 | 73.1 | 72.4 | 0.7 |

[a] Normal boiling temperatures [41]

[b] Experimental data from Table 2, from drop-calorimetry, transpiration method, and static method. Uncertainties are twice standard deviation

[c] Calculated using Eq. (8) with the assessed expanded uncertainty of ± 1.0 kJ mol$^{-1}$

[d] Difference between column 3 and 4 in this table

properties of halogen-substituted benzenes, for which experimental data are well established [26]. The enthalpies of vaporisation of the halogenated anisoles evaluated in this work (see Table 2) were correlated with the enthalpies of vaporisation of halogen-benzenes. Results of these correlations are given in Tables S20-S22 and very good linear correlations were obtained. The high correlations coefficients of theses linear correlations can be considered as an indicator for inherent consistency of the well-established data on halogen-substituted benzenes and the vaporisation enthalpies of halogen-substituted anisoles evaluated in this work. The results of the $\Delta^{g}_{l}H^{o}_{m}$(298.15 K) – (*S-P)* correlations are given Table 2 and they are labeled as (*S–P)*. As can be seen from this table, the vaporisation enthalpies derived from the (*S–P)* correlations are in a good agreement with those of the conventional methods.

The comprehensive evaluation and validation of the liquid–gas, solid–gas, and solid–liquid phase transition enthalpies of halogen-substituted anisoles has made it possible to estimate the weighted average value for each compound reported in Table 2 and to recommend the average values for thermochemical calculations. Now these values can be combined with the results of combustion calorimetry to obtain and discuss the *experimental* gas phase enthalpies of formation.

## Gas-phase standard molar enthalpies of formation: experiment and theory

The standard molar enthalpies of formation, $\Delta_{f}H^{o}_{m}$(liq or cr, 298.15 K), of *mono*-halogen-substituted and *di*-chloro-substituted anisoles were derived from the high-precision combustion calorimetry [12, 30, 32–34]. The available results are summarized in Table 10, column 2 and were combined together with the experimental results on vaporisation/sublimation enthalpies evaluated in Table 2 (see Table 10, column 3) to order to derive the *experimental* gas-phase standard molar enthalpies of formation $\Delta_{f}H^{o}_{m}(g)_{exp}$ (see Table 10, column 4). Since the available enthalpies of formation, $\Delta_{f}H^{o}_{m}$(liq or cr, 298.15 K), for halogen-substituted anisoles are limited to a single determination, we used quantum chemical (QC) calculations to ensure consistency and to support the reliability of the results collected in Table 10. Nowadays, the QC composite methods are a valuable tool for obtaining the *theoretical* values of $\Delta_{f}H^{o}_{m}$(g, 298.15) with a "chemical accuracy" (conventionally at the level of 4-5 kJ mol$^{-1}$) [56]. QC calculations of halogen-substituted anisoles were reported earlier using the DFT [30, 33, 57] and G3X [30, 33, 57] methods. In this work, we used G4 and G3MP2 methods to estimate the *theoretical* values of $\Delta_{f}H^{o}_{m}$(g, 298.15 K) halogen-substituted anisoles for validation of *experimental* results collected in Table 10. Using

**Table 10** The experimental, $\Delta_{f}H^{o}_{m}(g)_{exp}$, and theoretical standard molar gas-phase enthalpies of formation, $\Delta_{f}H^{o}_{m}(g)_{theor}$, of substituted anisoles at $T = 298.15$ K and $p° = 0.1$ MPa

| Compound | $\Delta_{f}H^{o}_{m}(liq)_{exp}$ [a]/kJ mol$^{-1}$ | $\Delta^{g}_{l,cr}H^{o}_{m}$ [b]/kJ mol$^{-1}$ | $\Delta_{f}H^{o}_{m}(g)_{exp}$/kJ mol$^{-1}$ | $\Delta_{f}H^{o}_{m}(g)_{theor}$ [c]/ kJ mol$^{-1}$ |
|---|---|---|---|---|
| 2-fluoro-anisole (liq) | − 301.9 ± 1.5 | 52.2 ± 0.7 | − 249.7 ± 1.7 | − 253.0 |
| 3-fluoro-anisole (liq) | − 314.5 ± 1.6 | 48.2 ± 0.4 | − 266.3 ± 1.6 | − 266.7 |
| 4-fluoro-anisole (liq) | − 309.2 ± 1.6 | 48.3 ± 0.4 | − 260.9 ± 1.6 | − 261.2 |
| 2-chloro-anisole (liq) | − 154.1 ± 1.8 | 55.9 ± 0.3 | − 98.2 ± 1.8 | − 94.7 |
| 3-chloro-anisole (liq) | − 160.2 ± 1.8 | 54.3 ± 0.3 | − 105.9 ± 1.8 | − 101.9 |
| 4-chloro-anisole (liq) | − 156.9 ± 1.8 | 54.4 ± 0.2 | − 102.5 ± 1.8 | − 99.2 |
| 2-bromo-anisole (liq) | − 101.5 ± 1.7 | 61.0 ± 0.7 | − 40.5 ± 1.8 | − 40.0 |
| 3-bromo-anisole (liq) | − 106.5 ± 1.7 | 57.9 ± 0.4 | − 48.6 ± 1.7 | − 45.5 |
| 4-bromo-anisole (liq) | − 106.7 ± 1.8 | 58.3 ± 0.4 | − 48.4 ± 1.8 | − 43.9 |
| 2-iodo-anisole (liq) | − 50.2 ± 1.6 | 65.2 ± 0.5 | 15.0 ± 1.7 | 16.0[d] |
| 3-iodo-anisole (liq) | − 50.7 ± 1.8 | 62.3 ± 0.6 | 11.6 ± 1.9 | 11.0[d] |
| 4-iodo-anisole (cr) | − 70.0 ± 1.4 | 81.4 ± 0.4 | 11.9 ± 1.5 | 11.9[d] |
| 2,3-*di*-chloro-anisole (cr) | − 201.3 ± 1.8 | 83.1 ± 0.5 | − 118.2 ± 1.9 | − 116.4 |
| 2,4-*di*-chloro-anisole (liq) | − 184.4 ± 1.7 | 61.8 ± 0.3 | − 122.6 ± 1.7 | − 120.5 |
| 2,6-*di*-chloro-anisole (liq) | − 165.4 ± 1.8 | 54.9 ± 0.3 | − 110.5 ± 1.8 | − 111.3 |
| 3,5-*di*-chloro-anisole (cr) | − 204.9 ± 1.8 | 80.1 ± 0.6 | − 124.8 ± 1.9 | − 129.4 |

Uncertainties in this table are expanded uncertainties 0.95 level of confidence with $k = 2$

[a] Experimental results from references [12, 30, 32–34]

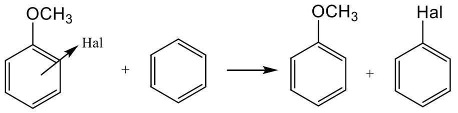
[b] Experimental results evaluated in Table 2

[c] Calculated using the G4 method and reactions R1 and R2

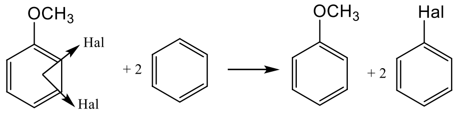
[d] Calculated using B3LYP/6-311+G(3d,p) [34]

two methods simultaneously helps to avoid possible systematic errors caused by the calculations. A correspondence between the *theoretical* and *experimental* values of $\Delta_f H_m^o$(g, 298.15 K) could provide valuable evidence of their mutual consistency.

Stable conformers were found by using a computer code named CREST (conformer-rotamer ensemble sampling tool) [58] and optimised with the B3LYP/6-31 g(d,p) method [59]. The energies $E_0$ and the enthalpies $H_{298}$ of the most stable conformers were finally calculated by using the G4 and G3MP2 methods. The $H_{298}$-values were converted to the standard molar enthalpies of formation $\Delta_f H_m^o$(g, 298.15 K) by using the enthalpies of the following well-balanced reactions R1 and R2:



Reaction R1



Reaction R2

The *theoretical* enthalpies of formation of halogen-substituted anisoles were calculated according to Hess´s law applied to reactions R1 and R2 using reliable enthalpies of formation of benzene, anisole, and halogen-substituted benzenes collected in Table S23. Results of QC calculations are summarised in Table 11. As can be seen from this table, the G4 and G3MP2 calculated gas phase formation enthalpies of the *mono*- and *di*-halogen-substituted anisoles are practically indistinguishable within 1.0 kJ mol$^{-1}$. Both methods also provide results in close agreement with experiment. Surprisingly, the DFT results are also very close to the gas phase formation enthalpies calculated by G4 and G3MP2. This is most probably due to sufficient errors cancellation specific to the well-balanced reactions R1 and R2. The good agreement of the G4 results with the experiment has prompted this method to be used for calculations of the enthalpies of formation of other *di*-halogenated anisoles (see Table 12) where experimental data are absent.

## Development of a "centerpiece" approach for substituted benzenes

Halogen substituted aromatics (anisoles, dioxines, phenols, naphthalenes etc.) are generally considered to be undesirable toxic pollutants, making it crucial to know

**Table 11** Comparison of experimental, $\Delta_f H_m^o(g)_{exp}$, and theoretical standard molar gas-phase enthalpies of formation, $\Delta_f H_m^o(g)_{theor}$, of substituted anisoles at $T = 298.15$ K and $p° = 0.1$ MPa

| Compound | $\Delta_f H_m^o(g)_{exp}$[a]/kJ mol$^{-1}$ | $\Delta_f H_m^o(g)_{G4}$[b]/kJ mol$^{-1}$ | $\Delta_f H_m^o(g)_{G3MP2}$[c]/kJ mol$^{-1}$ | $\Delta_f H_m^o(g)_{DFT}$/kJ mol$^{-1}$ |
|---|---|---|---|---|
| 2-fluoro-anisole | −249.7 ± 1.7 | −253.0 | | −251.0[d] [30] |
| 3-fluoro-anisole | −266.3 ± 1.6 | −266.7 | −268.6 | −265.5[d] [30] |
| | | | −266.9[f] [57] | −268.2[g] [57] |
| 4-fluoro-anisole | −260.9 ± 1.6 | −261.2 | | −260.7[d] [30] |
| 2-chloro-anisole | −98.2 ± 1.8 | −94.7 | −94.6 | |
| 3-chloro-anisole | −105.9 ± 1.8 | −101.9 | −101.1 | |
| 4-chloro-anisole | −102.5 ± 1.8 | −99.2 | −99.4 | |
| 2-bromo-anisole | −40.5 ± 1.8 | −40.0 | | −41.4[e] [33] |
| 3-bromo-anisole | −48.6 ± 1.7 | −45.5 | | −47.6[e] [33] |
| 4-bromo-anisole | −48.4 ± 1.8 | −43.9 | | −45.5[e] [33] |
| 2,3-*di*-chloro-anisole | −118.2 ± 1.9 | −116.4 | −116.9 | |
| 2,4-*di*-chloro-anisole | −122.6 ± 1.7 | −120.5 | −121.2 | |
| 2,6-*di*-chloro-anisole | −110.5 ± 1.8 | −111.3 | | |
| 3,5-*di*-chloro-anisole | −124.8 ± 1.9 | −129.4 | −129.4 | |
| 3,5-*di*-fluoro-anisole | | −465.2 | −460.7[f] [57] | −464.0[g] [57] |

Uncertainties in this table are expanded uncertainties 0.95 level of confidence with $k = 2$)

[a] From Table 10

[b] Calculated using the G4 method and reactions R1 and R2

[c] Calculated using the G3MP2 method and reactions R1 and R2

[d] Calculated using the B3LYP/6-311++G(d,p) and reaction R1 [30]

[e] Calculated using the B3LYP/6–311++G(d,p) and reaction R1 [33]

[f] Calculated using the B3LYP/6-311+G(3df,2p)/B3LYP/6-31G(d,p) and reactions R1 and R2 [57]

[g] Calculated using the G3X method and reactions R1 and R2 [57]

**Table 12** Theoretical gas-phase standard molar enthalpies of formation, $\Delta_f H^o_m(g)_{theor}$, of *di*-halogen-substituted anisoles at $T = 298.15$ K and $p° = 0.1$ MPa calculated using the G4 method

| Compound | $\Delta_f H^o_m(g)_{G4}$/ kJ mol$^{-1}$ |
|---|---|
| 3,5-*di*-fluoro-anisole | − 465.2 |
| 2,4-*di*-fluoro-anisole | − 446.6 |
| 2,5-*di*-fluoro-anisole | − 449.1 |
| 2,3-*di*-fluoro-anisole | − 435.9 |
| 2,6-*di*-fluoro-anisole | − 433.4 |
| 3,5-*di*-chloro-anisole | − 129.4 |
| 2,4-*di*-chloro-anisole | − 120.5 |
| 2,5-*di*-chloro-anisole | − 122.7 |
| 2,3-*di*-chloro-anisole | − 116.4 |
| 2,6-*di*-chloro-anisole | − 111.3 |
| 3,5-*di*-bromo-anisole | − 24.0 |
| 2,4-*di*-bromo-anisole | − 16.9 |
| 2,5-*di*-bromo-anisole | − 18.8 |
| 2,3-*di*-bromo-anisole | − 11.9 |
| 2,6-*di*-bromo-anisole | − 8.9 |
| 3,5-*di*-iodo-anisole | 98.8[a] |
| 2,4-*di*-iodo-anisole | 103.7[a] |
| 2,5-*di*-iodo-anisole | 102.5[a] |
| 2,3-*di*-iodo-anisole | 118.8[a] |
| 2,6-*di*-iodo-anisole | 119.0[a] |

[a] Calculated using the B3LYP/6-311G(d,p) method and reaction R2

their thermochemical properties, which are still extremely sparse. Predicting the thermochemical properties of these compounds is essential for evaluating their stability in air, water and soil. The variety of structural motifs of pollutants is too great to study their properties experimentally, therefore arbitrary calculations should be developed for this purpose. In our recent work, we develop the group additivity-based "centrepiece" approach [1–4] to predict vaporization enthalpies and formation enthalpies of organic molecules. The main idea is to select an appropriate "centrepiece" molecule (*e.g*. benzene, or anisole, or halogen-benzene, etc.) with well-established thermochemical properties. Different kinds of substituents can be attached to the "centrepiece" at different positions. To show a general example related to this work, let us consider the benzene as the "centrepiece" molecule. The thermochemical properties of benzene are precisely known [60]. The methoxy- and halogen-substituents can be appended to the benzene ring in the *ortho*-, *meta*-, or *para*-positions thereby formally constructing a framework of *mono*-, *di*-, or *poly*-halogen-substituted anisoles. The numerical enthalpic contribution for each appended to the benzene ring substituent is quantified as the differences between the enthalpy of the benzene itself and the enthalpy of the methoxy- or halogen-substituted benzene. The consistent sets of thermochemical data on vaporisation enthalpies, $\Delta^g_l H^o_m$(298.15 K) and gas-phase enthalpies of formation,$\Delta_f H^o_m$(g, 298.15 K), evaluated in this work for halogen-substituted anisoles have been used for development of the "centrepiece" approach that is particularly suitable for different types of aromatic compounds. Using this idea, the contributions $\Delta H(\mathrm{H} \rightarrow CH_3O)$, $\Delta H(\mathrm{H} \rightarrow \mathrm{F})$, $\Delta H(\mathrm{H} \rightarrow \mathrm{Cl})$, $\Delta H(\mathrm{H} \rightarrow \mathrm{Br})$, and $\Delta H(\mathrm{H} \rightarrow \mathrm{I})$were derived (see Table 13) using data for benzene, methoxybenzene, fluoro-, chloro-, bromo-, and iodo-benzene compiled in Table S23. Now these contributions $\Delta H(\mathrm{H} \rightarrow R)$are ready to build a framework of arbitrary structured halogen-substituted anisoles. However, in terms of energy, this framework needs to be extended to account for mutual interactions between the methoxy- and halogen-substituents on the benzene ring. Of course, the enthalpy contributions for these pairwise interactions of substituents are specific to the *ortho*-, *meta*-, and *para*-positions of the substituents appended to the benzene ring. As a rule, these interactions are quantified using the reaction enthalpies, $\Delta_r H^o_m$(g), according to reaction R1, written in reverse. This approach also applies to the estimation of contributions to the enthalpy of vaporization. The pairwise interactions derived in this way in terms of vaporisation and formation enthalpies are shown in Table 13 and they strongly depend on the type of the *ortho*-, *meta*- or *para*-substitution. It can be seen in Table 13, that all *ortho*-halogen-substituted anisoles exhibit a moderate destabilization of 3–12 kJ·mol$^{-1}$on their enthalpies of formation $\Delta_f H^o_m$(g), due to steric interactions of groups placed in close proximity. The *meta*- and *para*-interactions of substituents are numerically somewhat less intensive compared to *ortho*-interactions and exhibit a moderate stabilization or destabilization at from -1.3 to 4.2 kJ mol$^{-1}$ (see Table 13).

The nature of the pairwise substituent contributions with respect to $\Delta^g_l H^o_m$ is not apparent as they reflect peculiarities of the liquid structure. Nevertheless, these contributions must be used as empirical constants to obtain the correct enthalpies of vaporization for practical applications. For example, the following general formula for calculation of vaporisation enthalpy of any *poly*-halogen substituted anisoles (*HalA*) at 298.15 K can be suggested:

$$\begin{aligned}\Delta^g_l H^o_m(HalA) = {} & \Delta^g_l H^o_m(A) + n_a \times DH(H \rightarrow Hal) + n_b \times (ortho\text{-}Hal\text{-}Hal) + n_c \times (para\text{-}Hal\text{-}Hal) \\ & + n_d \times (meta\text{-}Hal\text{-}Hal) + n_e \times (ortho\text{-}Hal\text{-}OCH_3) + n_f \times (para\text{-}Hal\text{-}OCH_3) + n_g \times (meta\text{-}Hal\text{-}OCH_3)\end{aligned} \quad (9)$$

**Table 13** Parameters for the calculation of enthalpies of vaporisation and enthalpies of formation of halogen substituted anisoles at 298.15 K

| Parameter | $\Delta_l^g H_m^o$/kJ mol$^{-1}$ | $\Delta_f H_m^o$(g)/kJ mol$^{-1}$ | Parameter | $\Delta_l^g H_m^o$/kJ mol$^{-1}$ | $\Delta_f H_m^o$ (g)/ kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| *benzene* [60] | 33.9 | 82.9 | *ortho-Cl-(OCH$_3$)* | 1.6 | 5.7 |
| *ΔH(H→F)* [26, 61] | 0.8 | − 195.1 | *meta-Cl-(OCH$_3$)* | 0.0 | − 1.5 |
| *ΔH(H→Cl)* [26, 61] | 7.9 | − 30.1 | *para-Cl-(OCH$_3$)* | 0.1 | 1.2 |
| *ΔH(H→Br)* [26, 61] | 10.4 | 22.5 | | | |
| *ΔH(H→I)* [26, 61] | 14.9 | 83.2 | *ortho-Br-(OCH$_3$)* | 4.2 | 7.8 |
| *ΔH(H→OCH$_3$)* [4] | 12.5 | − 153.2 | *meta-Br-(OCH$_3$)* | 1.1 | 2.3 |
| | | | *para-Br-(OCH$_3$)* | 1.5 | 3.9 |
| *ortho-F-(OCH$_3$)* | 5.0 | 12.4 | *ortho-I-(OCH$_3$)* | 3.9 | 3.1 |
| *meta-F-(OCH$_3$)* | 1.0 | − 1.3 | *meta-I-(OCH$_3$)* | 1.0 | − 1.9 |
| *para-F-(OCH$_3$)* | 1.1 | 4.2 | *para-I-(OCH$_3$)* | 1.7 | − 1.0 |

where $\Delta_l^g H_m^o(A)$ is the vaporisation enthalpy of anisole; $\Delta H(H \rightarrow Hal)$ is an increment of $H \rightarrow Hal$ substitutions on the benzene ring. The mutual interactions of the *Hal* atoms were taken into account through the three types of corrections in *ortho*-, *para*-, and *meta*-position on the benzene ring, $n_a$, $n_b$, $n_c$, $n_d$. The mutual interactions between the *Hal* atoms and methoxy-group were taken into account through the three types of corrections in *ortho*-, *para*-, and *meta*-position on the benzene ring, $n_e$, $n_f$, $n_g$. The quantities of the corresponding increments and contributions specific for halogen-substituted anisoles are collected in Table 13. The quantities of the corresponding increments and contributions specific for halogen-substituted benzenes were determined in our previous work [61] and collected in Table S24. The uncertainties in estimating the enthalpies of vaporization are assessed at ± 1.5 kJ mol$^{-1}$ (double the standard deviation). The same algorithm as in Eq. (9) for enthalpies of vaporization can be used to estimate the of $\Delta_f H_m^o$(g)-values of halogen-substituted anisoles using the corresponding group additivity parameters given in Tables 13 and S25. The uncertainties in estimating the enthalpies of formation are assessed at ± 1.5 kJ mol$^{-1}$ (double the standard deviation). Some examples of group additive calculations and comparisons with experiments are given below.

Examples: vaporisation enthalpy, $\Delta_l^g H_m^o$(298.15 K), (in kJ mol$^{-1}$):
2,4-diCl-anisole: 62.4 ± 1.5 (additive) and 61.9 ± 0.5 (exp);
3,5-diCl-anisole: 60.7 ± 1.5 (additive) and 60.2 ± 0.5 (exp);
2,3-diCl-anisole: 62.5 ± 1.5 (additive) and 64.8 ± 0.3 (exp).

Examples: enthalpy of formation, $\Delta_f H_m^o$(g, 298.15 K), (in kJ mol$^{-1}$):
2,3-diCl-anisole: − 117.4 ± 2.0 (additive) and − 118.2 ± 1.9 (exp);
2,4-diCl-anisole: − 120.6 ± 2.0 (additive) and − 122.5 ± 1.7 (exp);
2,6-diCl-anisole: − 116.1 ± 2.0 (additive) and − 110.5 ± 1.8 (exp);
3,5-diCl-anisole: − 130.5 ± 2.0 (additive) and − 124.8 ± 1.9 (exp)

For estimations of the enthalpies of vaporization, it was found that the 1,2,3-sequences of substituents on the benzene ring might have an additional and individual contribution. For example, for the sequence Cl-CH$_3$O-Cl this contribution is − 9.0 kJ mol$^{-1}$ or for the sequence Br-CH$_3$O-Br − 5.5 kJ mol$^{-1}$. These contributions should be considered as the unique contributions and applied by estimations of vaporisation enthalpies. In contrast, the 1,2,3-sequences of substituents on the benzene ring for enthalpy of formation estimates show no additional energetic interactions within the experimental uncertainties. Thus, the collection of parameters from Tables 13, S24 and S25 allows for reasonable accuracy for the prediction of $\Delta_l^g H_m^o$(298.15 K) and $\Delta_f H_m^o$(g, 298.15 K) for halogen-substituted anisoles. Some limitations are to be expected in the case of 1,2,3,4-substitution, but the synthesis of such crowded benzenes is challenging, and samples are scarcely available for experimental study. Otherwise, success of the prediction with Eq. (9) could also be taken as evidence for the internal consistency of the experimental results on vaporization and formation enthalpies evaluated in Table 10.

## Conclusions

The enthalpies of vaporization/sublimation of halogen-substituted anisoles have been derived from the vapour pressures temperature dependences measured using the transpiration method, as well as derived from the solution calorimetry based approach. Experimental data on phase transition and formation enthalpies available in the literature were collected and analysed. The experimental results on the liquid–gas, solid–gas, and solid–liquid phase transition were evaluated using own complementary results and with empirical correlations based on boiling points and retention indices. The high-level quantum-chemical G4 and G3MP2 methods were validated with help of reliable experimental results and the gas-phase enthalpies of the formation of halogen-substituted anisoles were estimated. The evaluated set of thermodynamic data was used to design the "centerpiece" method for prediction vaporization and formation of halogen-substituted anisoles. The pairwise interactions of substituents on a benzene ring derived in this work should be transferrable to the assessment of the thermodynamic properties of halogen-substituted aromatics such as dioxins, phenols, naphthalenes, etc.

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## Declarations

**Conflict of interest** The authors declare no competing financial interest.

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