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# The energetics of the isomeric 1- and 2-naphthoic acids: context, quantum chemical calculations and thermochemical measurements

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**The isomeric 1- and 2-naphthoic acids are at the confluence of diverse concepts, techniques and classes of organic compounds. Summing the results of literature measurements of the enthalpy of formation of their solids and of our new sublimation enthalpies (using both the transpiration (transference) and combined correlation-gas chromatography–fusion enthalpy methods) reported herein, we derive gas phase enthalpies of formation of $-222.7 \pm 1.3$ and $-231.1 \pm 1.7$ kJ mol$^{-1}$. This corresponds to 2-naphthoic acid being more stable than its 1-isomer by 8.4 kJ mol$^{-1}$. We also performed MP2(full)/6-31G(d) calculations which resulted in enthalpies of formation of $-217.2 \pm 1.8$ and $-228.8 \pm 1.8$ kJ mol$^{-1}$ for 1- and 2-naphthoic acid and a difference of 11.6 kJ mol$^{-1}$, respectively. We are encouraged by the agreement between the results of contemporary thermochemical and computational theoretical practice.**

## 1. Introduction: concepts, context and compounds

The study of organic compounds is filled with concepts that are paired. Aromaticity and substituent effects are two key concepts. The study of the first has concentrated on hydrocarbons. The study of the second has, by definition, considered the replacement of hydrogen by some other functional group. Equilibria and rates are two other key concepts. The former relates to thermochemical concerns, to the energy (enthalpy, Gibbs free energy) differences between a pair of species. The latter is the province of kinetics, and relates to the ease of the interconversion of these two species. Inductive and resonance effects arise from all substituents and affect both equilibria and rates. The condensed phase and gases refer to yet another pair of concepts. Both relate to the neighbourhood of a molecule. Condensed phases, be they liquid or solid, have a high local concentration, where intermolecular interactions are inherent. The gas phase, ideally at least, assumes the molecule is isolated and intramolecular interactions are all that need to be considered and all that can be understood. Yet other concepts contain pairs. Hydrophobicity and hydrophilicity are among them. Hydrophobicity refers to the avoidance of water by some solute; hydrophilicity to bonding to water. However, one must consider interaction between the components of the bulk solute as well as between solute and water. Acidity and basicity are likewise paired. 'Acid' and 'base' are not quite antonyms or antithetical.

Benzoic acid has been a key substance for all of these concepts in organic chemistry. Benzoic acid is benzene with an affixed carboxyl group. Benzene is the archetypal aromatic hydrocarbon and carboxyl groups have been among the first functional groups to be introduced into a hydrocarbon—the Grignard reagent and its reaction with $CO_2$ among the simplest reactions to form a new C–C bond. Once formed, the newly affixed

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carbon in the carboxyl group could be modified to a plethora of other substituents. The Hammett $\sigma\rho$ analysis was among the first quantitative correlations in organic chemistry to quantify substituent effects on both equilibria and rates, and benzoic acid provided a key molecular framework for the disentangling of $\sigma$ and inductive effects from $\pi$ and resonance substituent effects. While it was necessary to introduce a variety of modified substituent constants, the underlying linear free energy principle remained intact. While the vast majority of chemical experiments were—and are—done in the condensed phase, in the pictures drawn by the organic chemist the models usually referred to isolated molecules. Only more recently were there corresponding experiments in the gas phase, by then accompanied by quantum chemical calculations on isolated molecules, and still later were there gas phase cluster experiments and models of solvation to help bridge the gap between the phases. A disproportionate number of these studies dealt with ions where solvation effects were larger and more important for even qualitative understanding. Benzoic acid is composed of a superbly hydrophobic part, the gloppy, greasy, benzene ring and a superbly hydrogen-bonding, water-solubilizing carboxyl group. The acidity of benzoic acid and its substituted derivatives was the property addressed in the pioneering $\sigma\rho$ analysis. As the name of the compound correctly says, benzoic acid is an acid, although in the absence of solvation, that is, in the gas phase, benzoic acid is both a stronger acid and a stronger base than water. Benzoic acid has been a key substance for all of these concepts in organic chemistry and more. This easily purified, easily obtained substance early on became an important experimental standard, 'benchmark' and calibration material for the calibration of experimental calorimetric measurements of all organic compounds.

Carboxylic acids are important to the biochemist and medicinal chemist: fatty acids, amino acids, prostaglandins and the Krebs cycle all come to mind. All of these are aliphatic or alicyclic. We must admit that while benzoic acid and other aromatic carboxylic acids have not been particularly prominent to date, two derivatives stand out with nearly unsurpassed relevance. The first species is the 2-acetoxybenzoic acid, widely known as the general analgesic, aspirin. The second derivative is *p*-aminobenzoic acid, which is a component of folic acid and so part of the $C_1$-machinery of cells. We also note that synthetic modifications of *p*-aminobenzoic acid and/or folic acid have had medicinal applications ranging from the anti-syphilitic salvarsan to the early antibiotic 'sulphur drugs' to the anti-cancer methotrexate. *p*-Aminobenzoic acid is also the carboxylic acid part of numerous components of 'sun blocks'. Generalizing to carboxylic acid derivatives of 1-ring (and thus including heterocyclic) aromatics, we include in the discussion 5′-phosphoribosyl-5-aminoimidazole-4-carboxylic acid, an important intermediate in purine synthesis. We should also not forget the food preservative sodium benzoate which is presumably protonated to form benzoic acid prior to digestion, metabolic detoxification and subsequent excretion.

Naphthalene is another standard for our understanding. Like benzoic acid, this easily purified, easily obtained species became an experimental standard for measurements and an archetype for concepts. With its two rings it became a stepping stone for the understanding of general polynuclear aromatic hydrocarbons. With its two benzene rings it became a paradigm, much more important than its isomer azulene (a later paradigm in its own right) and even more so than its (largely ignored 8:4 fused) isomers bicyclo[6.2.0.0[1,8]] decapentaene and (all-but-forgotten 9:3 fused) bicyclo [7.1.0.0[1,9]] decapentaene. Naphthalene is also a paradigm for steric interactions with its so-called *peri*-1 and -8 positions structurally but not electronically nearby, and for electronic phenomena such as the site specificity for electrophilic attack (1- (or $\alpha$) versus 2- (or $\beta$-)) and bond fixation (the Mills–Nixon effect). If the biological activity of naphthalene is usually discussed in the context of mothballs, we recall that many of the larger more-ringed polynuclear aromatic hydrocarbons such as the isomeric benz[a] and benz[e]pyrene are archetypes of carcinogenic and rather innocuous organic compounds, respectively.

The current study incorporates the above two chemical standards, benzoic acid and naphthalene and the confluence of the above diverse concepts and species. Substituted naphthalenes have also been investigated, albeit with much less intensity and interest than substituted benzenes. With a new armamentarium of experimental and calculational approaches, we consider—or rather reconsider—the isomeric 1- and 2-naphthoic acids (naphthalene-1- and -2-carboxylic acid). We will not attempt to re-enter all of the fields in which benzoic acid and naphthalene have been prominent. Rather, we limit our discussion to the enthalpies of formation of these two isomers, to test the accuracy and precision of our results from contemporary thermochemical and computational theoretical practice.

## 2. Compilation of results: literature and our own

Tables 1 and 2 give a compilation of the results from this work and those obtained from the literature for the enthalpies of sublimation of 1- and 2-naphthoic acids. As can be seen, there is excellent agreement between the values obtained in this work by transpiration and combined correlation-gas chromatography–fusion enthalpy measurements, with those obtained earlier by

Table 1. Enthalpy of sublimation of 1-naphthoic acid.

| Reference | Purification | Purity degree | $\Delta_{sub}H(\theta)$ | $\Delta_{sub}H$ (298.15 K) | Methodology |
|---|---|---|---|---|---|
| Colomina *et al.* [1] | Cryst. + subl. + z.r.m.[a] | >99.9% | 110.38 ± 0.21 (350.5 K) | 112.0 ± 0.6 | Knudsen effusion |
| Sabbah *et al.* [3] | | | 110.38 ± 0.21 (350.5 K) | 113.64 | |
| Holdiness [2] | z.r.m. | n.a.[b] | 117.6 ± 0.4 | | DSC |
| This work | Subl. + z.r.m. | 99.9% | | 109.89 ± 0.51 | Transpiration |
| This work | Subl. + z.r.m. | 99.9% | | 111.8 ± 7.8 | Combined correlation-gas chromatography–fusion enthalpy measurements |
| Mean weighted value | | | | 110.8 ± 0.8 | |

[a]z.r.m., zone refined material.
[b]n.a., not available.

Table 2. Enthalpy of sublimation of 2-naphthoic acid.

| Reference | Purification | Purity degree | $\Delta_{sub}H(\theta)$ | $\Delta_{sub}H$ (295.15 K) | Methodology |
|---|---|---|---|---|---|
| Colomina *et al.* [1] | Cryst. + subl. + z.r.m.[a] | >99.9% | 113.60 ± 0.79 (355.6 K) | 115.2 ± 0.8 | Knudsen effusion |
| Sabbah *et al.* [3] | | | 113.60 ± 0.79 (355.6 K) | 117.19 | |
| Holdiness [2] | z.r.m. | n.a.[b] | 119.5 ± 0.6 | | DSC |
| This work | Subl. + z.r.m. | 99.9% | | 114.87 ± 0.75 | Transpiration |
| This work | Subl. + z.r.m. | 99.9% | | 115.9 ± 6.7 | Combined correlation-gas chromatography–fusion enthalpy measurements |
| Mean weighted value | | | | 115.0 ± 0.9 | |

[a]z.r.m., zone refined material.
[b]n.a., not available.

Table 3. Compilation of the enthalpies of combustion and formation in the solid state of 1-naphthoic acid at $T = 298.15$ K.

| Reference | Purification | Purity degree | $\Delta_c H^\circ_m$(cr) KJ mol$^{-1}$ | $\Delta_f H^\circ_m$(cr) KJ mol$^{-1}$ |
|---|---|---|---|---|
| Colomina *et al.* [1] | Cryst. + subl. + z.r.m[a] | >99.9% | −5138.43 ± 0.87 | 333.5 ± 1.0 |
| Holdiness [2] | z.r.m. | n.a.[b] | −5150.92 ± 6.74 | |
| Balcan *et al.* [5] | | n.a. | −5110.71 ± 5.10 | |

[a]z.r.m., zone refined material.
[b]n.a., not available.

Colomina *et al.* [1] using the Knudsen effusion technique, but not with that obtained by Holdiness [2] using differential scanning calorimetry (DSC).

A weighted average was calculated [4] from the values of this work and that obtained earlier by Colomina *et al.* as $\mu = \sum(x_i\sigma_i^{-2})/(\sigma_i^{-2})$, where $x_i$ are the values of the enthalpies of sublimation at $T = 298.15$ K from each work, and $\sigma_i$ their corresponding uncertainties. The uncertainty associated with $\mu$ was calculated as $\sigma_s^2 = N\sigma_\mu^2$, with $\sigma_\mu^{-2} = \sum\sigma_i^{-2}$ and $N$ the number of individual contributing values. The value given by Sabbah and coworkers [3] was not considered in as much as it is taken from the experimental value given by Colomina *et al.* corrected at $T = 298.15$ K using adjustment for the temperature taken from the aminobenzoic acids.

Tables 3 and 4 collect the available data from the literature for the enthalpies of combustion and formation in the crystalline state of 1- and 2-naphthoic acids.

## 3. Computational details

Standard *ab initio* molecular orbital calculations [6] were performed with the Gaussian 98 series of programs [7]. For all the species included in this study, full geometry optimizations were carried out at the HF/6-31G(d) level, that is no assumptions were made as to planarity or to the value of any bond length or angle.

Table 4. Compilation of the enthalpies of combustion and formation in the solid state of 2-naphthoic acid at $T = 298.15$ K.

| Reference | Purification | Purity degree | $\Delta_c H^\circ_m$(cr) kJ mol$^{-1}$ | $\Delta_f H^\circ_m$(cr) kJ mol$^{-1}$ |
|---|---|---|---|---|
| Colomina *et al.* [1] | Cryst. + subl. + z.r.m.[a] | >99.9% | −5138.43 ± 0.87 | 346.1 ± 1.5 |
| Holdiness [2] | z.r.m. | n.a.[b] | −5137.95 ± 7.20 | |

[a] z.r.m., zone refined material.
[b] n.a., not available

Table 5. Electronic energies, ($E_{el}$), zero-point vibrational energies (ZPE), and thermal corrections to enthalpies (TCH) for all the compounds studied in this work. All values in hartrees.

| Compound | $E_{el}$[a] | ZPE[b,c] | TCH[b] |
|---|---|---|---|
| 1-naphthoic acid | −572.769 411 | 0.175 164 | 0.185 160 |
| 2-naphthoic acid | −572.773 611 | 0.174 981 | 0.184 941 |
| benzene | −231.487 188 | 0.107 669 | 0.112 708 |
| naphthalene | −384.664 605 | 0.158 155 | 0.165 395 |
| benzoic acid | −419.595 758 | 0.124 670 | 0.132 272 |

[a] Evaluated at the MP2(FULL)/6-31G(d) level.
[b] Evaluated at the HF/6-31G(d) level.
[c] Unscaled values.

The corresponding harmonic vibrational frequencies were evaluated at the same level of theory to confirm that the optimized structures found correspond to the minima of the potential energy surface and to evaluate the corresponding zero-point vibrational energies (ZPEs) and the thermal corrections at 298 K. ZPE values were scaled by the empirical factor 0.9135 [8]. All the minima found at the HF/6-31G(d) level were again fully reoptimized at the MP2(FULL)/6-31G(d) level.

Electronic energies, ZPEs, and thermal corrections to enthalpies for 1- and 2-naphthoic acids and other compounds used as references are collected in table 5.

The enthalpies of formation of the isomeric naphthoic acids have been calculated using the simple and direct homodesmotic reaction (1)

naphthalene + benzoic acid
⟶ (either 1- or 2-) naphthoic acid + benzene. (1)

Using for benzene [9], naphthalene [10],† and benzoic acid [11] the values of their enthalpies of formation taken from the literature, 82.7 ± 1.1, 150.5 ± 1.4, and −295.4 ± 0.2 kJ mol$^{-1}$, respectively, enthalpy of formation values of −217.2 ± 1.8, and −228.8 ± 1.8 kJ mol$^{-1}$ have been obtained for 1- and 2-naphthoic acids, respectively. As expected, the 1-isomer is less stable than its 2-counterpart presumably because the *peri*-(1,8-)H/COOH repulsion in the former species is much more destabilizing than the H/H repulsion in the latter: -COOH is larger than H.

†This value was taken from evaluation of the experimental available data from the literature, for the energies of combustion sublimation, vaporization, and fusion.

## 4. Experimental details: transpiration method

The enthalpies of sublimation of the two naphthoic acids (see table 6) were determined using the method of transference in a saturated $N_2$ stream. The method has been described before [12] and has given results in excellent agreement with other established techniques for determining vapour pressures of pure substances and enthalpies of vaporization from the temperature dependence of the vapour pressure. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of length 20 cm and diameter 0.5 cm. A nitrogen stream was passed through the U-tube at constant temperature (±0.1 K), and the transported amount of material was condensed in a cooled trap. The amount of condensed product was determined by gas chromatography analysis using an external standard (hydrocarbon). Assuming that Dalton's law of partial pressures of ideal gaseous mixtures applied to the saturated nitrogen stream is valid, values of the vapour pressure $p$ were calculated according to

$$p = mRT_a / V(N_2)M \quad (2)$$

where $R = 8.314\,51$ J K$^{-1}$ mol$^{-1}$, $m$ is the mass of transported compound, $V(N_2)$ the volume of transporting gas, $M$ the molar mass of the compound, and $T_a$ the temperature of the soap bubble meter. The volume $V(N_2)$ of the gas transferred through the tube was determined from the flow rate and time measurements. The vapour pressure $p$ at each saturation temperature was calculated from the mass of sample collected within a definite time period according to equation (2). The equation

$$R \ln(p) = a + \frac{b}{T} + \Delta^g_{cr} C_p \ln\left(\frac{T}{T_0}\right) \quad (3)$$

was fitted to the experimental $p,T$ data using $a$ and $b$ as adjustable parameters. The following equation gives the

Table 6. Results for the vapour pressure $p$ and $\Delta_{cr}^{g}H_m^\circ$ of 1-naphthoic acid by the transpiration method.

| $T$/K[a] | $m$/mg[b] | $V(N_2)$/dm$^3$[c] | $p$/Pa[d] | $(p_{exp}-p_{calc})$/Pa | $\Delta_{cr}^{g}H_m^\circ$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 1-Naphthoic acid; $\Delta_{cr}^{g}H_m^\circ(298.15\,K)=(109.89\pm0.51)$ kJ mol$^{-1}$ | | | | | |
| $\ln(p/Pa)=\frac{322.328}{R}-\frac{119046.212}{R(T/K)}-\frac{30.70}{R}\ln\left(\frac{T/K}{298.15}\right)$ | | | | | |
| 332.9 | 0.074 | 107.7 | 0.0098 | 0.000 | 108.83 |
| 338.2 | 0.184 | 151.9 | 0.0174 | 0.000 | 108.67 |
| 340.0 | 0.091 | 59.90 | 0.0217 | 0.000 | 108.61 |
| 343.3 | 0.219 | 96.83 | 0.0324 | 0.001 | 108.51 |
| 343.5 | 0.457 | 200.6 | 0.0325 | 0.001 | 108.50 |
| 345.9 | 0.221 | 74.82 | 0.0423 | 0.001 | 108.43 |
| 348.2 | 0.461 | 122.7 | 0.0537 | 0.000 | 108.36 |
| 348.4 | 0.214 | 54.25 | 0.0563 | 0.002 | 108.35 |
| 351.0 | 0.212 | 40.40 | 0.0751 | 0.003 | 108.27 |
| 351.2 | 0.102 | 19.88 | 0.0731 | 0.000 | 108.27 |
| 354.2 | 0.254 | 35.35 | 0.1027 | 0.002 | 108.17 |
| 354.2 | 0.802 | 121.5 | 0.0943 | −0.006 | 108.17 |
| 357.6 | 0.231 | 23.99 | 0.1377 | −0.005 | 108.07 |
| 357.6 | 0.573 | 62.14 | 0.1317 | −0.011 | 108.07 |
| 358.2 | 0.108 | 10.64 | 0.1456 | −0.006 | 108.05 |
| 360.1 | 0.257 | 20.41 | 0.1800 | −0.003 | 107.99 |
| 360.4 | 1.288 | 102.0 | 0.1805 | −0.009 | 107.98 |
| 363.1 | 0.466 | 26.72 | 0.2490 | 0.002 | 107.90 |
| 363.7 | 0.289 | 16.52 | 0.2502 | −0.012 | 107.88 |
| 365.2 | 0.272 | 13.55 | 0.2868 | −0.017 | 107.84 |
| 366.3 | 0.260 | 11.15 | 0.3333 | −0.004 | 107.80 |
| 366.7 | 0.377 | 15.02 | 0.3591 | 0.008 | 107.79 |
| 367.2 | 0.311 | 11.78 | 0.3768 | 0.009 | 107.77 |
| 369.3 | 0.240 | 7.20 | 0.4762 | 0.026 | 107.71 |
| 372.4 | 0.284 | 6.44 | 0.6301 | 0.027 | 107.62 |
| 374.4 | 0.475 | 9.30 | 0.7291 | 0.003 | 107.55 |
| 375.3 | 0.275 | 5.05 | 0.7781 | −0.010 | 107.53 |
| 376.4 | 0.245 | 3.91 | 0.8952 | 0.023 | 107.49 |
| 377.3 | 0.227 | 3.41 | 0.9530 | 0.007 | 107.46 |
| 378.4 | 0.299 | 4.04 | 1.057 | 0.012 | 107.43 |
| 380.4 | 0.302 | 3.37 | 1.281 | 0.030 | 107.37 |

[a] Temperature of saturation. $N_2$ gas flow 0.82 to 1.44 cm$^3$ s$^{-1}$.
[b] Mass of transferred sample condensed at $T=273$ K.
[c] Volume of nitrogen used to transfer mass $m$ of sample.
[d] Vapour pressure at temperature $T$ calculated from $m$ and the residual vapour pressure at $T=273$ K.

value of the sublimation enthalpy at temperature $T$:

$$\Delta_{cr}^{g}H_m^\circ(T) = -b + \Delta_{cr}^{g}C_p T. \qquad (4)$$

$T_0$ appearing in equation (3) is an arbitrarily chosen reference temperature, here chosen as 298.15 K.

The results for 1- and 2-naphthoic acid together with their corresponding parameters $a$ and $b$ are listed in tables 6 and 7, respectively. Values of $\Delta_{cr}^{g}C_p$ have been derived from the isobaric molar heat capacities $C_p$(cr) of solid naphthalene derivatives and from values of the isobaric molar heat capacities $C_p$(g) of gaseous species calculated according to a procedure developed by Domalski and Hearing [13].

Table 7. Results for the vapour pressure $p$ and $\Delta_{cr}^{g}H_m^\circ$ of 2-naphthoic acid by the transpiration method.

| $T$/K[a] | $m$/mg[b] | $V(N_2)$/dm$^3$[c] | $p$/Pa[d] | $(p_{exp}-p_{calc})$/Pa | $\Delta_{cr}^{g}H_m^\circ$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 2-Naphthoic acid; $\Delta_{cr}^{g}H_m^\circ(298.15\,K)=(114.87\pm0.75)$ kJ mol$^{-1}$ | | | | | |
| $\ln(p/Pa)=\frac{334.456}{R}-\frac{124024.048}{R(T/K)}-\frac{30.70}{R}\ln\left(\frac{T/K}{298.15}\right)$ | | | | | |
| 335.1 | 0.072 | 117.9 | 0.009 | 0.000 | 113.74 |
| 338.3 | 0.214 | 239.4 | 0.013 | 0.000 | 113.64 |
| 340.2 | 0.265 | 223.6 | 0.017 | 0.001 | 113.58 |
| 343.4 | 0.207 | 124.3 | 0.024 | 0.000 | 113.48 |
| 348.4 | 0.247 | 84.24 | 0.042 | 0.000 | 113.33 |
| 350.5 | 0.275 | 73.93 | 0.053 | 0.000 | 113.27 |
| 352.5 | 0.390 | 83.98 | 0.067 | 0.001 | 113.20 |
| 355.7 | 0.276 | 44.24 | 0.090 | −0.004 | 113.11 |
| 358.5 | 0.337 | 41.64 | 0.116 | −0.010 | 113.02 |
| 361.6 | 0.336 | 27.39 | 0.176 | 0.001 | 112.92 |
| 364.6 | 0.379 | 22.40 | 0.243 | 0.005 | 112.83 |
| 367.7 | 0.451 | 19.50 | 0.333 | 0.007 | 112.74 |
| 370.7 | 0.885 | 28.08 | 0.454 | 0.014 | 112.65 |
| 373.5 | 0.540 | 13.61 | 0.571 | −0.007 | 112.56 |

[a] Temperature of saturation. $N_2$ gas flow 0.82 to 1.44 cm$^3$ s$^{-1}$.
[b] Mass of transferred sample condensed at $T=273$ K.
[c] Volume of nitrogen used to transfer mass $m$ of sample.
[d] Vapour pressure at temperature $T$ calculated from $m$ and the residual vapour pressure at $T=273$ K.

## 5. Experimental details: combined correlation-gas chromatography–fusion enthalpy measurements

Sublimation enthalpies were also obtained by summing the experimental fusion enthalpy adjusted to 298 K with the vaporization enthalpy also at 298 K measured by correlation-gas chromatography [14]. Enthalpies of transfer from solution to the vapour were calculated from the retention times of each solute adjusted for the dead volume of the column. Methylene chloride was used as the non-retained reference. Table 8 summarizes the thermochemical properties of the standards used in this part of our study.

A plot of the corrected retention time ($t_{solute} - t_{CH_2Cl_2}$) versus $1/T$ (K$^{-1}$) resulted in linear plots from which values of $-\Delta_{sln}^{g}H_m(T_m)$ were calculated for each of the standards and unknowns as the product of the slope and gas constant $R$. The retention times and values of $\Delta_{sln}^{g}H_m(T_m)$ for all the analytes associated with 1-naphthoic acid are tabulated in tables 9 and 10, while the corresponding data for 2-napthoic acid are given in tables 11 and 12.

A plot of the vaporization enthalpies of the standards, $\Delta_{vap}H_m(298.15\,K)$ against the corresponding values of $\Delta_{sln}^{g}H_m(T_m)$, resulted in the linear relationships reported at the bottom of tables 10 and 12. Values of $\Delta_{vap}H_m$ (298.15 K) for both 1- and 2-naphthoic acids were obtained from the appropriate correlation equation and their respective $\Delta_{sln}^{g}H_m(T_m)$. The resulting vaporization

Table 8. Thermochemical properties of the vaporization enthalpy standards used in correlation gas chromatography.

| | $\Delta_{vap}H_m(T_m/K)$ kJ mol$^{-1}$ | $T_m$/K | $C_{Pm}(l)(298.15\,K)$ J mol$^{-1}$ K$^{-1}$ | $\Delta_{vap}H_m(298.15K)$ kJ mol$^{-1}$ | Reference |
|---|---|---|---|---|---|
| benzoic acid | 69.2 | 395.5 | 211.7 | 75.6[a] | 16 |
| 4-ethylbenzoic acid | | | 272 | 88.5[b] | 17–9 |
| decanoic acid | 88.6 | 314 | 377.5 | 90.3[a] | 22 |
| undecanoic acid | 90.7 | 323 | 409.4 | 93.6[a] | 22 |
| pentadecanoic acid | 108.5 | 357 | 537 | 117.3[a] | 22 |

[a]Adjusted to 298.15 K using the following relationship: $\Delta_{vap}H_m\,(298.15K) = \Delta_{vap}H_m(T_m) + [10.58 + 0.26C_p(l)][T_m - 298.15\,K]$ [15].
[b]Calculated from an average of the sublimation enthalpies reported in the literature (98.2 kJ mol$^{-1}$, 298.15 K) [17, 18] by subtracting the fusion enthalpy (14.06 kJ mol$^{-1}$; $T_{fus}$ 386.2 K) [19], adjusted to 298.15 K using estimated heat capacities ($C_p$(cr) 203.7; $C_p$(l) 272 J mol$^{-1}$ K$^{-1}$) and equation (5) [20, 21].

Table 9. Gas chromatographic retention times $t_r$/min of 1-naphthoic acid.

| $T$/K | 423.8 | 428.7 | 433.6 | 438.5 | 443.3 | 448.2 | 453.1 |
|---|---|---|---|---|---|---|---|
| *Run 1* | | | | $t_r$/min | | | |
| $CH_2Cl_2$ | 0.221 | 0.231 | 0.233 | 0.235 | 0.232 | 0.240 | 0.242 |
| benzoic acid | 0.792 | 0.730 | 0.674 | 0.625 | 0.576 | 0.547 | 0.518 |
| 4-ethylbenzoic acid | 1.823 | 1.602 | 1.410 | 1.252 | 1.115 | 1.010 | 0.919 |
| decanoic acid | 1.750 | 1.530 | 1.343 | 1.180 | 1.055 | 0.953 | 0.865 |
| undecanoic acid | 2.730 | 2.336 | 2.010 | 1.743 | 1.520 | 1.345 | 1.197 |
| 1-naphthoic acid | 7.653 | 6.418 | 5.403 | 4.587 | 3.920 | 3.371 | 2.925 |
| pentadecanoic acid | 17.755 | 14.244 | 11.480 | 9.355 | 7.685 | 6.343 | 5.290 |
| $T$/K | 423.75 | 428.65 | 433.65 | 438.45 | 443.35 | 448.25 | 453.05 |
| *Run 2* | | | | $t_r$/min | | | |
| $CH_2Cl_2$ | 0.22 | 0.223 | 0.21 | 0.225 | 0.23 | 0.231 | 0.233 |
| benzoic acid | 0.785 | 0.716 | 0.64 | 0.606 | 0.564 | 0.53 | 0.5 |
| 4-ethylbenzoic acid | 1.805 | 1.578 | 1.363 | 1.222 | 1.089 | 0.983 | 0.894 |
| decanoic acid | 1.727 | 1.5 | 1.292 | 1.155 | 1.027 | 0.925 | 0.838 |
| undecanoic acid | 2.69 | 2.294 | 1.944 | 1.697 | 1.48 | 1.305 | 1.159 |
| 1-naphthoic acid | 7.571 | 6.325 | 5.275 | 4.477 | 3.808 | 3.272 | 2.829 |
| pentadecanoic acid | 17.517 | 14.006 | 11.218 | 9.124 | 7.462 | 6.16 | 5.125 |

Table 10. The vaporization enthalpies obtained by correlation-gas chromatography, the corresponding correlation equations and literature values.

| | $\Delta^g_{sln}H_m(T_m)$ kJ mol$^{-1}$ | | $\Delta_{vap}H_m(298.15\,K)$ kJ mol$^{-1}$ | $\Delta_{vap}H_m(298.15\,K)$ kJ mol$^{-1}$ calculated | | |
|---|---|---|---|---|---|---|
| Compound | Run 1 | Run 2 | Literature | Run 1 | Run 2 | Mean |
| benzoic acid | 39.8 | 40.9 | 75.6 | 76.3 | 76.3 | 76.3 |
| 4-ethylbenzoic acid | 47.1 | 47.8 | 88.5 | 86.9 | 86.5 | 86.7 ± 0.2 |
| decanoic acid | 49.0 | 49.8 | 90.3 | 89.8 | 89.4 | 89.6 ± 0.2 |
| undecanoic acid | 52.7 | 53.5 | 93.6 | 95.1 | 94.9 | 95.0 ± 0.1 |
| 1-naphthoic acid | 55.6 | 56.8 | | 99.3 | 99.6 | 99.5 ± 0.2 |
| pentadecanoic acid | 67.9 | 68.8 | 117.3 | 117.2 | 117.3 | 117.3 ± 0.1 |

$\Delta_{vap}H_m(298.15\,K) = (1.453 \pm 0.066)\Delta^g_{sln}H_m(T_m) + (18.5 \pm 1.39)$; $r^2 = 0.9938$ (Run 1)
$\Delta_{vap}H_m(298.15\,K) = (1.466 \pm 0.054)\Delta^g_{sln}H_m(T_m) + (16.42 \pm 1.11)$; $r^2 = 0.9960$ (Run 2)

enthalpies are summarized in the sixth column of table 13.

Fusion enthalpies of 1- and 2-naphthoic acid were obtained from the literature and adjusted to 298.15 K using equation (5) and the estimated isobaric molar heat capacities of the liquid and solid listed in table 13. The vaporization enthalpies measured by correlation gas chromatography are also given in this table.

Table 11. Gas chromatographic retention times $t_r$/min of 2-naphthoic acid.

| $T$/K | 423.75 | 428.65 | 433.65 | 438.45 | 443.25 | 448.25 | 453.05 |
|---|---|---|---|---|---|---|---|
| *Run 1* | | | | $t_r$/min | | | |
| $CH_2Cl_2$ | 0.223 | 0.225 | 0.225 | 0.225 | 0.229 | 0.229 | 0.229 |
| benzoic acid | 0.78 | 0.713 | 0.655 | 0.605 | 0.563 | 0.53 | 0.496 |
| 4-ethylbenzoic acid | 1.792 | 1.565 | 1.372 | 1.216 | 1.085 | 0.98 | 0.885 |
| decanoic acid | 1.732 | 1.505 | 1.312 | 1.159 | 1.025 | 0.925 | 0.833 |
| undecanoic acid | 2.682 | 2.282 | 1.955 | 1.692 | 1.476 | 1.3 | 1.152 |
| 2-naphthoic acid | 8.018 | 6.608 | 5.569 | 4.683 | 3.98 | 3.407 | 2.924 |
| pentadecanoic acid | 17.481 | 13.985 | 11.21 | 9.089 | 7.445 | 6.146 | 5.108 |
| $T$/K | 423.75 | 428.65 | 433.65 | 438.45 | 443.35 | 448.25 | 453.15 |
| *Run 2* | | | | $t_r$/min | | | |
| $CH_2Cl_2$ | 0.224 | 0.22 | 0.226 | 0.225 | 0.225 | 0.226 | 0.232 |
| benzoic acid | 0.787 | 0.711 | 0.66 | 0.607 | 0.562 | 0.531 | 0.5 |
| 4-ethylbenzoic acid | 1.805 | 1.564 | 1.382 | 1.221 | 1.089 | 0.982 | 0.89 |
| decanoic acid | 1.754 | 1.5 | 1.324 | 1.165 | 1.035 | 0.926 | 0.836 |
| undecanoic acid | 2.697 | 2.284 | 1.967 | 1.699 | 1.481 | 1.305 | 1.159 |
| 2-naphthoic acid | 8.063 | 6.71 | 5.586 | 4.707 | 4.005 | 3.43 | 2.947 |
| pentadecanoic acid | 17.563 | 14.033 | 11.247 | 9.134 | 7.484 | 6.18 | 5.139 |

Table 12. The vaporization enthalpies obtained by correlation-gas chromatography, the corresponding correlation equations and literature values.

| | $\Delta^g_{sln}H_m(T_m)$ kJ mol$^{-1}$ | | $\Delta_{vap}H_m$(298.15 K) kJ mol$^{-1}$ | $\Delta_{vap}H_m$(298.15 K) kJ mol$^{-1}$ calculated | | |
|---|---|---|---|---|---|---|
| Compound | Run 1 | Run 2 | Literature | Run 1 | Run 2 | Mean |
| benzoic acid | 39.9 | 40 | 75.6 | 75.8 | 75.7 | 76.8 ± 0.1 |
| 4-ethylbenzoic acid | 47.4 | 47.5 | 88.5 | 86.5 | 86.5 | 86.5 |
| decanoic acid | 49.9 | 50.1 | 90.3 | 90.0 | 90.3 | 90.2 ± 0.2 |
| undecanoic acid | 53.3 | 53.3 | 93.6 | 95.0 | 94.8 | 94.9 ± 0.1 |
| 1-naphthoic acid | 57.6 | 57.6 | | 101.0 | 101.1 | 101.1 ± 0.1 |
| pentadecanoic acid | 68.8 | 68.7 | 117.3 | 117.0 | 117.0 | 117 |

$\Delta_{vap}H_m(298.15\,K) = (1.428 \pm 0.05)\,\Delta^g_{sln}H_m(T_m) + (18.78 \pm 1.09)$; $r^2 = 0.9962$ (Run 1)
$\Delta_{vap}H_m(298.15\,K) = (1.441 \pm 0.053)\,\Delta^g_{sln}H_m(T_m) + (18.09 \pm 1.12)$; $r^2 = 0.9960$ (Run 2)

Table 13. Thermochemical properties of 1- and 2-naphthoic acid by correlation gas chromatography;[a] enthalpies in kJ mol$^{-1}$.

| $\Delta_{fus}H_m(T_{fus}/K)$ | $T_{fus}$/K | $C_p$(l)(298.15 K)[b] J mol$^{-1}$ K$^{-1}$ | $C_p$(cr)(298.15 K)[b] J mol$^{-1}$ K$^{-1}$ | $\Delta_{fus}H_m$ (298.15 K) | $\Delta_{vap}H_m$ (298.15 K) | $\Delta_{sub}H_m$ (298.15 K) |
|---|---|---|---|---|---|---|
| 19.89 [18] | 435.2 | 285.7 | 201.1 | 12.5 ± 2.4 | 99.4 ± 6.7 | 111.8 ± 7.2 |
| 23.54 [18] | 460.2 | 285.7 | 201.1 | 14.8 ± 2.8 | 101.1 ± 6.7 | 115.9 ± 6.7 |

[a]Uncertainty in the vaporization enthalpy calculated from the uncertainty in the slope of the correlation equation; the uncertainty in the fusion enthalpy is one-third of the temperature adjustment; both are ($\pm 2\sigma$).
[b]Estimated by group additivity [21].

Table 14. Enthalpies of formation and sublimation of the isomeric naphthoic acids at 298.15 K (kJ mol$^{-1}$).

| | Experimental | | | Calculated $\Delta_fH^\circ_m(g)$ | |
|---|---|---|---|---|---|
| | $\Delta_fH^\circ_m$(cr) | $\Delta_{sub}H^\circ_m$ | $\Delta_fH^\circ_m(g)$ | MP2(full)/6-31G(d) | $\Delta^a$ |
| 1-naphthoic acid | −333.5 ± 1.0 | 110.8 ± 0.8 | −222.7 ± 1.3 | −217.2 ± 1.8 | Exp: 8.4 |
| 2-naphthoic acid | −346.1 ± 1.5 | 115.0 ± 0.9 | −231.1 ± 1.7 | −228.8 ± 1.8 | Calc: 11.6 |

[a]$\Delta$ is defined as the difference of the enthalpies of formation of the gaseous naphthoic acids, $\Delta_fH^\circ_m$ (g, 1-naphthoic acid) − $\Delta_fH^\circ_m$ (g, 2-naphthoic acid) (kJ mol$^{-1}$).

$$\Delta_{fus}H_m(298.15K) = \Delta_{fus}H_m(T_{fus}/K) + [0.15C_p(cr) - 0.26C_p(l) - 9.83][T_{fus} - 298.15\,K]. \quad (5)$$

The sublimation enthalpy listed in the last column of table 13 represents the sum of these two enthalpies.

## 6. Summary: enthalpy of formation values and conclusion

Table 14 summarizes the experimental and calculated values for the enthalpies of formation in the gas state at $T = 298.15$ K.

The experimental values were calculated from the experimental values for the enthalpies of formation in the crystalline state of 1- and 2-naphthoic acids given by Colomina *et al.* [1] and the weighted average values of the enthalpies of sublimation of these compounds obtained in the present work. It is seen that the various experimental combustion, phase change enthalpy measurements, theoretical quantum chemical methods, and qualitative organic chemical assumptions are all in accord. We are not surprised. We are, nonetheless, pleased.

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