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# Enthalpies of formation of methyl substituted naphthalenes

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ABSTRACT

In this work, the enthalpies of formation for the homologous series of methyl substituted naphthalene isomers were calculated using the AM1, PM3, B3PW91, and G3MP2 methods. This work was done primarily to address the lack of data available for many of these compounds and to find the most cost-effective method to calculate the enthalpy of formation. In addition, we explored the development of a group-additivity model as a fast method to calculate the enthalpy of formation. Using this model, two sets of interaction parameters were derived. One set from the G3MP2 results and the other from the B3PW91 results. These parameters differ by an average of 2.3 kJ mol$^{-1}$, implying that the simpler B3PW91 calculations may be used to develop a group-additivity model. The model using the G3MP2 derived parameters deviate from the experimental values with a RMS of 3.0 kJ mol$^{-1}$. Using the B3PW91 parameters, the model has an RMS of 9.1 kJ mol$^{-1}$.

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## 1. Introduction

Compilations of basic physical property data exist for thousands of compounds [1–3]; however, it is infeasible, for many reasons, including cost, manpower, and experimental difficulty, to measure the properties of every existing and newly created compound. In response to these limitations, and to increase the understanding of the underlying chemistry, multiple calculation and estimation methods have been developed to predict the physical properties of compounds. The enthalpy of formation is one of these basic properties and describes the amount of energy contained in a molecule. Knowing the enthalpy of formation allows a chemist to determine many other molecular properties, including reactivity and the reduction–oxidation potential [4,5].

In this work, the standard enthalpies of formation ($\Delta H_f{}^{\circ}{}_{298}$) for all eighty-nine members of the homologous series of methyl substituted benzene and naphthalene isomers have been calculated using semi-empirical and *ab initio* methods. We have evaluated these methods for their accuracy, speed, and ease of calculation. The prime motivation for this work was to address the lack of data available for the methyl substituted naphthalenes. Of the seventy-six naphthalene compounds, only seven have had their enthalpies of formation experimentally measured and thirty-four have no physical property measurements reported in the literature [1–3]. A secondary driver for this work was to explore the development of a group-additivity model for aromatic compounds.

Group-additivity models, first developed by Benson, are fast, back-of-the envelope calculations that perform well for many series of compounds [6]. Their main drawback is that to develop these models, each group must be defined and the interactions between groups must be quantified. Previously, Whiteside and Carreira attempted to improve Benson's group additivity method for predicting the enthalpy of formation of hydrocarbons and extend it to include aromatic compounds [5,6]. This predictive work was successful for the compounds studied; however, verifying it as a general technique was difficult due to the lack of experimental measurements with which to compare the results. Also, since the group additivity parameters are based on experimental data, the interaction parameters cannot be determined for classes of compounds lacking this data. As a solution to this lack of data, we have performed calculations, whose results were used to extend the group additivity parameters and to predict the $\Delta H_f{}^{\circ}{}_{298}$ of methyl substituted naphthalenes and benzenes.

## 2. Theory

The Gaussian 03 software package [7] was used to calculate the $\Delta H_f{}^{\circ}{}_{298}$ using the AM1 [8], PM3 [9,10], B3PW91 6-31++G(d,p) [11,12], and G3MP2 methods [13]. The semi-empirical AM1 and PM3 methods were used as baselines against which to compare the other methods. The B3PW91 and G3MP2 methods were used as they are the most rigorous computations of these compounds that we could perform on our system. We chose the B3PW91 DFT functional as it fulfills the uniform electron gas limit and shows improvement over B3LYP for predicting atomization energies and hydrocarbon bond dissociation energies [14,15]. Using the G3MP2

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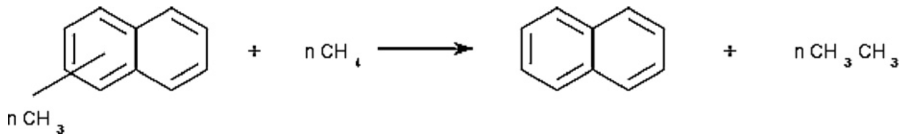
**Table 1**
Methyl substituted benzenes. Experimental and calculated $\Delta H_f{}^{\circ}{}_{298}$ values in kJ mol$^{-1}$.

| Name | CAS | Expt. | Reference | AM1 | PM3 | B3PW91 6–31++G(d,p) | | G3MP2 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | iso[a] | homo[b] | iso[a] | homo[b] |
| Benzene | 71-43-2 | 82.9 ± 0.0 | 3 | 91.7 | 97.8 | 82.9 | 82.9 | 82.9 | 82.9 |
| 1-Methylbenzene | 108-88-3 | 50.1 ± 1.1 | 3 | 59.8 | 58.5 | 55.4 | 50.1 | 50.2 | 50.1 |
| 1,2-Dimethylbenzene | 95-47-6 | 19.0 ± 1.1 | 3 | 30.5 | 22.6 | 29.8 | 19.3 | 16.8 | 16.5 |
| 1,3-Dimethylbenzene | 108-38-3 | 17.2 ± 0.8 | 3 | 28.1 | 19.4 | 28.3 | 17.8 | 17.7 | 17.4 |
| 1,4-Dimethylbenzene | 106-42-3 | 17.9 ± 1.0 | 3 | 27.8 | 19.3 | 26.1 | 15.5 | 18.3 | 18.0 |
| 1,2,3-Trimethylbenzene | 526-73-8 | −9.6 ± 1.3 | 3 | 4.3 | −12.5 | 10.4 | −5.4 | −10.9 | −11.3 |
| 1,2,4-Trimethylbenzene | 95-63-6 | −13.9 ± 1.1 | 3 | −1.2 | −16.4 | 0.5 | −15.3 | −15.3 | −15.7 |
| 1,3,5-Trimethylbenzene | 108-67-8 | −15.9 ± 1.5 | 3 | −3.5 | −19.5 | 1.1 | −14.7 | −14.8 | −15.2 |
| 1,2,3,4-Tetramethylbenzene | 488-23-3 | −37.6 ± 1.2 | 3 | −21.8 | −46.6 | −8.6 | −29.7 | −38.2 | −38.7 |
| 1,2,3,5-Tetramethylbenzene | 527-53-7 | −44.4 ± 1.2 | 3 | −27.3 | −51.4 | −16.5 | −37.5 | −42.8 | −43.3 |
| 1,2,4,5-Tetramethylbenzene | 95-93-2 | −47.1 ± 1.9 | 3 | −30.4 | −52.9 | −22.1 | −43.2 | −48.3 | −48.8 |
| 1,2,3,4,5-Pentamethylbenzene | 700-12-9 | −67.2 ± 2.2 | 3 | −47.4 | −83.1 | −26.7 | −53.0 | −65.0 | −65.6 |
| 1,2,3,4,5,6-Hexamethylbenzene | 87-85-4 | −77.4 ± 2.5 | 3 | −61.9 | −109.4 | −26.7 | −58.3 | −77.6 | −78.4 |

[a] These values calculated using the isodesmic equation, Eq. (3).
[b] These values calculated using the homodesmotic equation, Eq. (4).

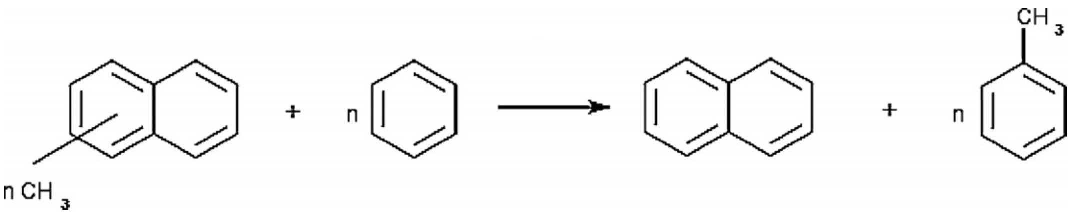
method, the largest compounds required a 64-bit operating system and used up to 3.3GB RAM, 96GB scratch space, and 30.3 hrs of CPU time on a 2.8 GHz AMD Opteron Processor.

We used isodesmic [16] and homodesmic [17] reactions and calculations to determine the enthalpy of formation of these compounds when using the B3PW91 and G3MP2 methods; the AM1 and PM3 methods provide the enthalpy of formation directly. An isodesmic reaction has the same number and type of bonds on each side of the equation. A homodesmic reaction is an isodesmic reaction where there are equal numbers of each type of carbon–carbon bond (sp$^3$–sp$^3$, sp$^3$–sp$^2$, sp$^3$–sp, etc.) in the reactants and products and there are equal numbers of each type of carbon atom (sp$^3$, sp$^2$, sp) with zero, one, two, and three hydrogens attached in the reactants and products [18]. These types of reactions result in values that are nearly size independent because correlation effects are canceled out and they make use of accurate experimental data [17–19]. Since the compounds studied are a homologous series, we were able to use the same reaction for each compound and simply alter the stoichiometric quantities (*n*). The isodesmic reaction was of the form:



(1)

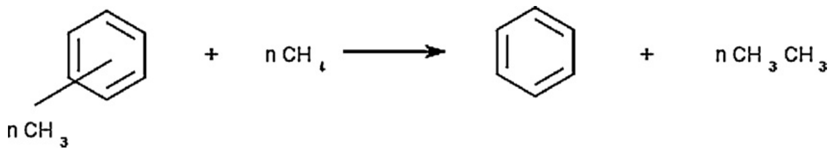
and the homodesmic form of this reaction is:



(2)

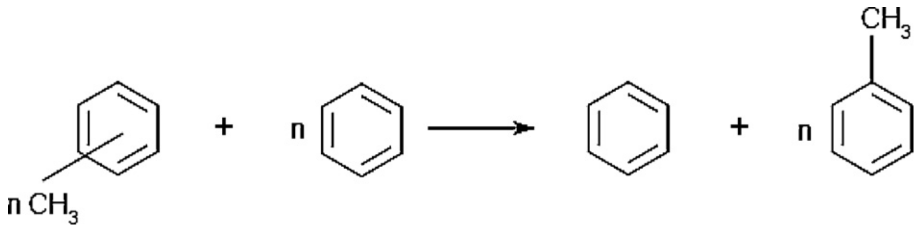
The values of the enthalpies of formation used in these equations are: naphthalene 150.6 kJ mol$^{-1}$; methane −74.6 kJ mol$^{-1}$; ethane −84.0 kJ mol$^{-1}$; toluene 50.1 kJ mol$^{-1}$; and benzene 82.9 kJ mol$^{-1}$ and were obtained from the NIST webbook [3].

We verified and validated this method by using the isodesmic equation:



(3)

and the homodesmotic equation:



(4)

**Table 2a**

Methyl substituted naphthalenes. Experimental and calculated $\Delta H_f{}^{\circ}{}_{298}$ values in kJ mol$^{-1}$.

| Name | CAS | Expt. | Reference | AM1 | PM3 | B3PW91 6-31++G(d,p) | | G3MP2 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | iso[a] | homo[b] | iso[a] | homo[b] |
| Naphthalene | 91-20-3 | 150.6 ± 1.1 | 3 | 169.1 | 169.5 | 150.6 | 150.6 | 150.6 | 150.6 |
| 1-Methylnaphthalene | 90-12-0 | 116.9 ± 2.7 | 3 | 141.3 | 135.7 | 126.4 | 121.7 | 117.8 | 117.7 |
| 2-Methylnaphthalene | 91-57-6 | 116.1 ± 2.6 | 3 | 136.8 | 129.9 | 122.2 | 117.6 | 116.6 | 116.4 |
| 1,2-Dimethylnaphthalene | 573-98-8 | | | 115.3 | 104.1 | 108.1 | 97.0 | 90.9 | 90.7 |
| 1,3-Dimethylnaphthalene | 575-41-7 | | | 109.1 | 96.2 | 98.0 | 86.9 | 83.6 | 83.4 |
| 1,4-Dimethylnaphthalene | 571-58-4 | | | 113.7 | 102.4 | 102.8 | 91.7 | 85.6 | 85.4 |
| 1,5-Dimethylnaphthalene | 571-61-9 | | | 113.9 | 102.5 | 102.7 | 91.7 | 85.5 | 85.3 |
| 1,6-Dimethylnaphthalene | 575-43-9 | | | 109.0 | 96.1 | 98.1 | 87.0 | 83.9 | 83.6 |
| 1,7-Dimethylnaphthalene | 575-37-1 | | | 109.8 | 97.0 | 98.0 | 87.0 | 83.8 | 83.5 |
| 1,8-Dimethylnaphthalene | 569-41-5 | 108.8 ± 3.0 | 3 | 133.4 | 115.7 | 130.4 | 119.3 | 111.0 | 110.7 |
| 2,3-Dimethylnaphthalene | 581-40-8 | 79.9 ± 1.1 | 3 | 108.0 | 94.7 | 96.9 | 85.8 | 83.2 | 82.9 |
| 2,6-Dimethylnaphthalene | 581-42-0 | 78.6 ± 1.8 | 3 | 104.6 | 90.4 | 94.1 | 83.0 | 82.8 | 82.6 |
| 2,7-Dimethylnaphthalene | 582-16-1 | 79.5 ± 0.6 | 3 | 104.6 | 90.4 | 94.1 | 83.0 | 82.7 | 82.4 |
| 1,2,3-Trimethylnapthalene | 879-12-9 | | | 91.0 | 62.8 | 89.53 | 72.9 | 63.6 | 63.2 |
| 1,2,4-Trimethylnapthalene | 2717-42-2 | | | 88.0 | 65.0 | 84.6 | 68.0 | 58.6 | 58.3 |
| 1,2,5-Trimethylnapthalene | 641-91-8 | | | 87.9 | 65.0 | 84.6 | 68.0 | 58.5 | 58.2 |
| 1,2,6-Trimethylnapthalene | 3031-05-8 | | | 83.0 | 58.5 | 80.0 | 63.4 | 57.0 | 56.7 |
| 1,2,7-Trimethylnapthalene | 486-34-0 | | | 83.9 | 58.6 | 80.1 | 63.5 | 57.0 | 56.6 |
| 1,2,8-Trimethylnapthalene | 3876-97-9 | | | 110.3 | 83.1 | 115.2 | 98.6 | 86.2 | 85.8 |
| 1,6,7-Trimethylnapthalene | 2245-38-7 | | | 80.2 | 60.9 | 72.7 | 56.0 | 50.1 | 49.7 |
| 2,3,6-Trimethylnapthalene | 829-26-5 | | | 75.8 | 55.2 | 69.0 | 52.4 | 49.5 | 49.1 |
| 1,3,8-Trimethylnapthalene | 17057-91-9 | | | 101.1 | 76.2 | 101.8 | 85.2 | 76.2 | 75.9 |
| 1,4,5-Trimethylnapthalene | 2131-41-1 | | | 107.6 | 84.3 | 109.3 | 92.7 | 80.7 | 80.3 |
| 1,3,5-Trimethylnapthalene | 2131-39-7 | | | 81.8 | 63.1 | 74.7 | 58.1 | 51.0 | 50.7 |
| 1,3,6-Trimethylnapthalene | 3031-08-1 | | | 76.9 | 56.6 | 69.7 | 53.1 | 49.7 | 49.4 |
| 1,3,7-Trimethylnapthalene | 2131-38-6 | | | 77.7 | 57.5 | 70.0 | 53.4 | 47.6 | 47.2 |
| 1,4,6-Trimethylnapthalene | 2131-42-2 | | | 82.2 | 63.7 | 74.5 | 57.9 | 49.9 | 49.5 |
| 1,2,4,5-Tetramethylnapthalene | 99486-62-1 | | | 82.0 | 47.1 | 90.62 | 68.5 | 53.1 | 52.6 |
| 1,2,7,8-Tetramethylnapthalene | 99486-64-3 | | | 85.0 | 51.1 | 99.48 | 77.3 | 60.7 | 60.2 |
| 1,2,6,7-Tetramethylnapthalene | 99486-63-2 | | | 54.3 | 29.4 | 54.7 | 32.6 | 23.5 | 23.0 |
| 1,2,4,8-Tetramethylnapthalene | 66577-22-8 | | | 84.3 | 52.2 | 94.01 | 71.9 | 55.4 | 54.9 |
| 1,2,4,6-Tetramethylnapthalene | 66577-21-7 | | | 56.5 | 25.6 | 56.36 | 34.2 | 23.2 | 22.7 |
| 1,2,3,6-Tetramethylnapthalene | 66577-20-6 | | | 58.7 | 23.3 | 61.26 | 39.1 | 29.7 | 29.2 |
| 1,2,6,8-Tetramethylnapthalene | 66577-00-2 | | | 78.1 | 43.6 | 88.04 | 65.9 | 51.5 | 51.0 |
| 1,2,3,7-Tetramethylnapthalene | 51958-56-6 | | | 59.6 | 23.3 | 61.73 | 39.6 | 29.7 | 29.2 |
| 1,2,3,4-Tetramethylnapthalene | 3031-15-0 | | | 75.9 | 31.8 | 84.86 | 62.7 | 48.5 | 48.0 |
| 1,2,5,7-Tetramethylnapthalene | 38157-33-4 | | | 56.7 | 25.7 | 56.43 | 34.3 | 24.3 | 23.8 |
| 1,3,5,8-Tetramethylnapthalene | 14558-12-4 | | | 75.5 | 44.9 | 80.56 | 58.4 | 45.8 | 45.3 |
| 1,4,6,7-Tetramethylnapthalene | 13764-18-6 | | | 55.8 | 27.7 | 49.21 | 27.1 | 17.8 | 17.3 |
| 1,2,3,5-Tetramethylnapthalene | 13093-32-8 | | | 63.6 | 29.6 | 66.34 | 44.2 | 31.0 | 30.5 |
| 1,3,6,7-Tetramethylnapthalene | 7435-50-9 | | | 48.1 | 21.5 | 44.77 | 22.6 | 16.1 | 15.6 |
| 1,3,5,7-Tetramethylnapthalene | 7383-94-0 | | | 50.5 | 23.8 | 46.77 | 24.6 | 17.3 | 16.8 |
| 1,2,5,8-Tetramethylnapthalene | 3031-16-1 | | | 84.1 | 52.0 | 93.92 | 71.8 | 55.5 | 55.0 |
| 1,2,5,6-Tetramethylnapthalene | 2131-43-3 | | | 62.0 | 39.6 | 66.15 | 44.0 | 31.4 | 30.9 |
| 2,3,6,7-Tetramethylnapthalene | 1134-40-3 | | | 47.0 | 20.1 | 44.17 | 22.0 | 16.3 | 15.8 |
| 1,2,3,8-Tetramethylnapthalene | 1079-07-8 | | | 84.7 | 49.2 | 97.1 | 75.0 | 57.7 | 57.2 |
| 1,4,5,8-Tetramethylnapthalene | 2717-39-7 | | | 104.6 | 70.7 | 119.61 | 97.5 | 80.1 | 79.6 |
| 1,2,4,7-Tetramethylnapthalene | 16020-17-0 | | | 56.5 | 32.4 | 56.33 | 34.2 | 23.3 | 22.8 |
| 1,3,6,8-Tetramethylnapthalene | 14558-14-6 | | | 68.9 | 36.7 | 72.63 | 50.5 | 41.5 | 41.0 |

[a] These values calculated using the isodesmic equation, Eq. (1).

[b] These values calculated using the homodesmotic equation, Eq. (2).

to calculate the energies of the homologous series of methyl substituted benzene isomers and compared those results with the experimental values (Table 1). There was good agreement between the experimental and computational results. However, these results show that as the number of atoms in a molecule increases, the accuracy of the simpler methods (AM1, PM3, B3PW91 isodesmic, B3PW91 homodesmic) decreases sharply. The root-mean squared (RMS) deviation of these calculations from the experimental values are 13.8 kJ mol$^{-1}$, 11.7 kJ mol$^{-1}$, 24.3 kJ mol$^{-1}$, and 7.5 kJ mol$^{-1}$, respectively, while the G3MP2 method has a RMS value of 1.2 kJ mol$^{-1}$ (isodesmic) and 1.3 kJ mol$^{-1}$ (homodesmic).

After validating the method, we calculated the enthalpies of formation of the homologous series of methyl substituted naphthalene isomers (Table 2) using the same computational methods and the homodesmic and isodesmic reactions described by Eqs. (1) and (2).

## 3. Discussion

This work compiles the calculated and measured enthalpy of formation data for all of the methyl substituted naphthalenes and benzenes into a single source. We have calculated the enthalpies of formation using the Gaussian 03 modeling programs and the AM1, PM3, B3PW91, and G3MP2 methods. For the B3PW91 and G3MP2 methods, the enthalpies of formation were calculated using both the isodesmic and homodesmic reactions. The results from the methyl substituted napthalene calculations are presented in Tables 2a and 2b.

**Table 2b**
Methyl substituted naphthalenes. Experimental and calculated $\Delta H_f{}^{\circ}{}_{298}$ values in kJ mol$^{-1}$.

| Name | CAS | Expt. | Reference | AM1 | PM3 | B3PW91 6-31++G(d,p) | | G3MP2 | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | iso[a] | homo[b] | iso[a] | homo[b] |
| 1,2,3,4,6-Pentamethylnapthalene | 56908-79-3 | | | 43.7 | −6.8 | 57.0 | 29.4 | 14.9 | 14.3 |
| 1,2,3,4,5-Pentamethylnapthalene | 56908-78-2 | | | 71.3 | 21.0 | 95.2 | 67.5 | 45.3 | 44.7 |
| 1,2,3,5,7-Pentamethylnapthalene | 209978-64-3 | | | 32.4 | −9.8 | 38.4 | 10.7 | −2.9 | −3.5 |
| 1,2,3,6,7-Pentamethylnapthalene | 209978-63-2 | | | 30.0 | −11.9 | 36.8 | 9.1 | −3.6 | −4.2 |
| 1,2,3,5,6-Pentamethylnapthalene | 209978-62-1 | | | 37.7 | −8.0 | 48.3 | 20.6 | 4.1 | 3.5 |
| 1,2,4,6,7-Pentamethylnapthalene | 171083-67-3 | | | 30.1 | −9.7 | 35.3 | 7.6 | −9.1 | −9.8 |
| 1,2,4,6,8-Pentamethylnapthalene | 92556-54-2 | | | 52.1 | 12.8 | 65.2 | 37.5 | 18.5 | 17.9 |
| 1,2,3,5,8-Pentamethylnapthalene | 92556-53-1 | | | 58.4 | 18.2 | 75.3 | 47.6 | 26.9 | 26.3 |
| 1,2,4,5,6-Pentamethylnapthalene | 68844-46-2 | | | 58.2 | 14.9 | 75.0 | 47.3 | 28.1 | 27.4 |
| 1,2,4,5,8-Pentamethylnapthalene | 2928-64-5 | | | 79.2 | 38.5 | 105.1 | 77.4 | 54.8 | 54.1 |
| 1,2,3,6,8-Pentamethylnapthalene | 66577-20-6 | | | 52.5 | 9.7 | 68.3 | 40.6 | 24.9 | 24.3 |
| 1,2,3,7,8-Pentamethylnapthalene | 1164113-50-1 | | | 59.0 | 17.1 | 79.2 | 51.5 | 31.6 | 30.9 |
| 1,2,4,5,7-Pentamethylnapthalene | 1103580-53-5 | | | 49.9 | 7.8 | 61.8 | 34.1 | 18.2 | 17.6 |
| 1,2,4,7,8-Pentalmethylnapthalene | 1164113-56-7 | | | 58.6 | 20.1 | 77.0 | 49.3 | 29.3 | 28.6 |
| 1,2,3,4,5,6-Hexamethylnapthalene | 56908-83-9 | | | 45.1 | −10.3 | 76.2 | 43.0 | 16.9 | 16.1 |
| 1,2,3,4,5,7-Hexamethylnapthalene | 56908-77-1 | | | 39.2 | −18.3 | 67.0 | 33.8 | 10.9 | 10.1 |
| 1,2,3,4,6,7-Hexamethylnapthalene | 17384-76-8 | | | 14.9 | −42.9 | 31.9 | −1.3 | −18.5 | −19.2 |
| 1,2,3,5,6,7-Hexamethylnapthalene | 51958-57-7 | | | 13.5 | −43.4 | 29.9 | −3.3 | −23.0 | −23.7 |
| 1,2,3,5,6,8-Hexamethylnapthalene | 872010-01-0 | | | 32.6 | −17.4 | 57.3 | 24.1 | 1.1 | 0.4 |
| 1,2,3,5,7,8-Hexamethylnapthalene | 1164113-71-6 | | | 32.6 | −14.0 | 57.3 | 24.0 | −0.2 | −0.9 |
| 1,2,3,6,7,8-Hexamethylnapthalene | 1164113-72-7 | | | 33.0 | −15.1 | 59.4 | 26.2 | 2.4 | 1.6 |
| 1,2,3,4,5,8-Hexamethylnapthalene | 36230-30-5 | | | 65.4 | 15.9 | 105.7 | 72.5 | 41.6 | 40.8 |
| 1,2,4,5,6,8-Hexamethylnapthalene | 1164113-75-0 | | | 53.7 | 5.6 | 87.7 | 54.5 | 27.9 | 27.1 |
| 1,2,4,5,7,8-Hexamethylnapthalene | 1164113-78-3 | | | 52.5 | 5.5 | 84.9 | 51.7 | 24.7 | 24.0 |
| 1,2,3,4,5,6,8-Heptamethylnapthalene | 259743-98-1 | | | 38.4 | −19.2 | 85.2 | 46.5 | 11.4 | 10.5 |
| 1,2,3,4,5,6,7-Heptamethylnapthalene | 56908-82-8 | | | 19.2 | −44.3 | 57.6 | 18.8 | −12.4 | −13.3 |
| 1,2,3,4,5,6,7,8-Octamethylnapthalene | 18623-61-5 | | | 22.4 | −39.1 | 81.4 | 37.1 | −5.8 | −6.8 |

[a] These values calculated using the isodesmic equation, Eq. (1).
[b] These values calculated using the homodesmotic equation, Eq. (2).

We compared the accuracy of the methyl substituted napthalene results, obtained from the isodesmic and homodesmic reactions for both the G3MP2 and B3PW91 calculations, to the experimental values. Using the G3MP2 calculated values, the enthalpy of formation determined by the isodesmic and homodesmic reactions are greater than the experimental enthalpy of formation by an average of 3.4 kJ mol$^{-1}$ and 3.3 kJ mol$^{-1}$, respectively. For the B3PW91 calculated values, the enthalpy of formation determined by the isodesmic and homodesmic reactions are greater than the experimental enthalpy of formation by an average of 14.5 kJ mol$^{-1}$ and 6.0 kJ mol$^{-1}$, respectively. From these results and those of the methyl substituted benzenes it is clear that the homodesmic reaction provides a more accurate method of calculating the enthalpy of formation when using lower levels of theory.

The enthalpies of formation values calculated by the AM1and PM3 methods are greater than the experimental values of the naphthalene series by an average of 24.7 kJ mol$^{-1}$ and 14.9 kJ mol$^{-1}$, respectively. When compared to the homodesmic G3MP2 values, the values obtained by these methods are greater by an average of 29.3 kJ mol$^{-1}$ and 13.2 kJ mol$^{-1}$.

It is well known that energies computed by DFT functionals are flawed by systematic errors, which can become considerable for larger molecules [19]. This is the exact trend we found when we compared the homodesmic B3PW91 results to the homodesmic G3MP2 results. The B3PW91 results are greater than the G3MP2 results by an average of 15.7 kJ mol$^{-1}$.

While the G3MP2 results are the most accurate, they are also the most computationally expensive. In the pharmaceutical industry, this expense is prohibitive for screening the large numbers of compounds in their drug libraries. So, these companies and other industrial players turn to other methods to determine the properties of interest. One of these methods is group additivity. As described previously, the group additivity method determines the number and types of groups in a molecule, looks up the values assigned to each group, and sums these values together [6]. This method is fast, simple, and accurate; however, its accuracy is low for complex molecules because values are assigned to each group, not to the interactions between groups. The attempt to overcome this limitation by assigning values to the group interactions was the driving force for the Whiteside and Carreria paper [5]. While that work was successful for the compounds studied, it was limited by the lack of experimental data available to determine the group interactions.

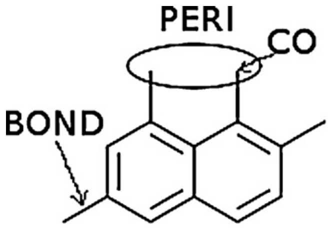


**Fig. 1.** Methyl interactions in benzene or naphthalene.

**Table 3**
Group additivity parameters, in kJ mol$^{-1}$, for methyl substituted benzene and naphthalene compounds.

| Name | Description | Value (G3MP2) | Value (B3PW91) |
|---|---|---|---|
| Methane base value | | −74.9 | −74.9 |
| Benzene base value | | 82.9 | 82.9 |
| Naphthalene base value | | 150.6 | 150.6 |
| BOND | $CH_3$–$CH_2$ bond energy | 41.4 | 43.1 |
| CO | Constrained ortho group | 6.9 | 9.0 |
| PERI | Peri interaction | 15.0 | 18.1 |

**Table 4a**
Group additivity results for the methyl substituted benzenes. All $\Delta H_f{}^{\circ}{}_{298}$ values in kJ mol$^{-1}$.

| Name | $\Delta H_f{}^{\circ}{}_{298}$ calc (G3MP2) | Methyl | Nap | BOND | CO | $\Delta H_f{}^{\circ}{}_{298}$ calc (GA) | $\Delta$ ($\Delta H_f{}^{\circ}{}_{298}$) |
|---|---|---|---|---|---|---|---|
| Benzene | 82.9 | 0 | 1 | 0 | 0 | 82.9 | 0.0 |
| 1-Methylbenzene | 50.2 | 1 | 1 | 1 | 0 | 48.7 | 1.5 |
| 1,2-Dimethylbenzene | 16.8 | 2 | 1 | 2 | 0 | 16.0 | 0.8 |
| 1,3-Dimethyl | 17.7 | 2 | 1 | 2 | 0 | 14.5 | 3.2 |
| 1,4-Dimethylbenzene | 18.3 | 2 | 1 | 2 | 0 | 14.5 | 3.7 |
| 1,2,3-Trimethylbenzene | −10.9 | 3 | 1 | 3 | 1 | −10.6 | −0.3 |
| 1,2,4-Trimethylbenzene | −15.3 | 3 | 1 | 3 | 0 | −18.2 | 2.9 |
| 1,3,5-Trimethylbenzene | −14.8 | 3 | 1 | 3 | 0 | −19.7 | 4.9 |
| 1,2,3,4-Tetramethylbenzene | −38.2 | 4 | 1 | 4 | 2 | −37.2 | −1.1 |
| 1,2,3,5-Tetramethylbenzene | −42.8 | 4 | 1 | 4 | 1 | −4.8 | 1.9 |
| 1,2,4,5-Tetramethylbenzene | −48.3 | 4 | 1 | 4 | 0 | −50.9 | 2.7 |
| 1,2,3,4,5-Pentamethylbenzene | −65.0 | 5 | 1 | 5 | 3 | −63.7 | −1.2 |
| 1,2,3,4,5,6-Hexamethylbenzene | −77.6 | 6 | 1 | 6 | 6 | −76.5 | −1.1 |

Here, we have calculated the group additivity interaction parameters for methyl substituted benzene and naphthalene compounds. While simple for “straight-chain” aromatics (benzene, naphthalene, anthracene, etc.), other aromatic compounds (phenanthrene, pyrene, etc.) have multiple interactions and enumerating them consistently and elucidating their values becomes exponentially more difficult. For this reason, it is an open question of whether calculating the compounds values using a high-level of theory or developing a comprehensive group additivity method is the more efficient and accurate method. The developed group

**Table 4b**
Group additivity results for the 0-4 methyl substituted naphthalenes. All $\Delta H_f{}^{\circ}{}_{298}$ values in kJ mol$^{-1}$.

| Name | $\Delta H_f{}^{\circ}{}_{298}$ calc (G3MP2) | Methyl | Nap | BOND | CO | PERI | $\Delta H_f{}^{\circ}{}_{298}$ calc (GA) | $\Delta$ ($\Delta H_f{}^{\circ}{}_{298}$) |
|---|---|---|---|---|---|---|---|---|
| Naphthalene | 150.6 | 0 | 1 | 0 | 0 | 0 | 150.6 | 0.0 |
| 1-Methylnaphthalene | 117 | 1 | 1 | 1 | 0 | 0 | 117.0 | 0.0 |
| 2-Methylnaphthalene | 118.3 | 1 | 1 | 1 | 0 | 0 | 118.5 | −0.2 |
| 1,2-Dimethylnaphthalene | 84.5 | 2 | 1 | 2 | 1 | 0 | 84.8 | −0.3 |
| 1,3-Dimethylnaphthalene | 83.6 | 2 | 1 | 2 | 0 | 0 | 83.3 | 0.3 |
| 1,4-Dimethylnaphthalene | 83.8 | 2 | 1 | 2 | 0 | 0 | 83.3 | 0.5 |
| 1,5-Dimethylnaphthalene | 84.1 | 2 | 1 | 2 | 0 | 0 | 84.7 | −0.6 |
| 1,6-Dimethylnaphthalene | 86.5 | 2 | 1 | 2 | 0 | 0 | 86.4 | 0.1 |
| 1,7-Dimethylnaphthalene | 111.9 | 2 | 1 | 2 | 0 | 1 | 114.9 | −3.0 |
| 1,8-Dimethylnaphthalene | 91.9 | 2 | 1 | 2 | 0 | 0 | 92.5 | −0.6 |
| 2,3-Dimethylnaphthalene | 86.6 | 2 | 1 | 2 | 0 | 0 | 86.4 | 0.2 |
| 2,6-Dimethylnaphthalene | 84.8 | 2 | 1 | 2 | 0 | 0 | 84.8 | 0.0 |
| 2,7-Dimethylnaphthalene | 84.7 | 2 | 1 | 2 | 0 | 0 | 84.8 | −0.1 |
| 1,2,3-Trimethylnapthalene | 65 | 3 | 1 | 3 | 2 | 0 | 66.4 | −1.4 |
| 1,2,4-Trimethylnapthalene | 60 | 3 | 1 | 3 | 1 | 0 | 60.3 | −0.3 |
| 1,2,5-Trimethylnapthalene | 59.9 | 3 | 1 | 3 | 1 | 0 | 60.3 | −0.4 |
| 1,2,6-Trimethylnapthalene | 58.45 | 3 | 1 | 3 | 1 | 0 | 58.8 | −0.4 |
| 1,2,7-Trimethylnapthalene | 58.36 | 3 | 1 | 3 | 1 | 0 | 58.8 | −0.5 |
| 1,2,8-Trimethylnapthalene | 87.56 | 3 | 1 | 3 | 1 | 1 | 88.8 | −1.3 |
| 1,6,7-Trimethylnapthalene | 51.49 | 3 | 1 | 3 | 0 | 0 | 52.6 | −1.1 |
| 2,3,6-Trimethylnapthalene | 50.87 | 3 | 1 | 3 | 0 | 0 | 51.1 | −0.2 |
| 1,3,8-Trimethylnapthalene | 77.64 | 3 | 1 | 3 | 0 | 1 | 81.2 | −3.6 |
| 1,4,5-Trimethylnapthalene | 82.1 | 3 | 1 | 3 | 0 | 1 | 82.7 | −0.6 |
| 1,3,5-Trimethylnapthalene | 52.44 | 3 | 1 | 3 | 0 | 0 | 52.7 | −0.3 |
| 1,3,6-Trimethylnapthalene | 51.15 | 3 | 1 | 3 | 0 | 0 | 51.2 | −0.1 |
| 1,3,7-Trimethylnapthalene | 49.01 | 3 | 1 | 3 | 0 | 0 | 51.2 | −2.2 |
| 1,4,6-Trimethylnapthalene | 51.27 | 3 | 1 | 3 | 0 | 0 | 52.7 | −1.5 |
| 1,2,4,5-Tetramethylnapthalene | 55.03 | 4 | 1 | 4 | 1 | 1 | 56.7 | −1.7 |
| 1,2,7,8-Tetramethylnapthalene | 62.57 | 4 | 1 | 4 | 2 | 1 | 62.8 | −0.2 |
| 1,2,6,7-Tetramethylnapthalene | 25.39 | 4 | 1 | 4 | 1 | 0 | 26.6 | −1.2 |
| 1,2,4,8-Tetramethylnapthalene | 57.33 | 4 | 1 | 4 | 1 | 1 | 56.7 | 0.6 |
| 1,2,4,6-Tetramethylnapthalene | 25.03 | 4 | 1 | 4 | 1 | 0 | 26.7 | −1.7 |
| 1,2,3,6-Tetramethylnapthalene | 31.58 | 4 | 1 | 4 | 2 | 0 | 32.8 | −1.2 |
| 1,2,6,8-Tetramethylnapthalene | 53.39 | 4 | 1 | 4 | 1 | 1 | 55.2 | −1.8 |
| 1,2,3,7-Tetramethylnapthalene | 31.6 | 4 | 1 | 4 | 2 | 0 | 32.8 | −1.2 |
| 1,2,3,4-Tetramethylnapthalene | 50.41 | 4 | 1 | 4 | 4 | 0 | 48.1 | 2.3 |
| 1,2,5,7-Tetramethylnapthalene | 26.19 | 4 | 1 | 4 | 1 | 0 | 26.7 | −0.5 |
| 1,3,5,8-Tetramethylnapthalene | 47.66 | 4 | 1 | 4 | 0 | 1 | 49.1 | −1.4 |
| 1,4,6,7-Tetramethylnapthalene | 19.65 | 4 | 1 | 4 | 0 | 0 | 20.5 | −0.9 |
| 1,2,3,5-Tetramethylnapthalene | 51.27 | 4 | 1 | 4 | 2 | 0 | 34.3 | 17.0 |
| 1,3,6,7-Tetramethylnapthalene | 18.02 | 4 | 1 | 4 | 0 | 0 | 19.0 | −1.0 |
| 1,3,5,7-Tetramethylnapthalene | 19.13 | 4 | 1 | 4 | 0 | 0 | 19.1 | 0.0 |
| 1,2,5,8-Tetramethylnapthalene | 57.38 | 4 | 1 | 4 | 1 | 1 | 56.7 | 0.7 |
| 1,2,5,6-Tetramethylnapthalene | 33.3 | 4 | 1 | 4 | 2 | 0 | 34.3 | −1.0 |
| 2,3,6,7-Tetramethylnapthalene | 18.17 | 4 | 1 | 4 | 0 | 0 | 18.9 | −0.7 |
| 1,2,3,8-Tetramethylnapthalene | 59.55 | 4 | 1 | 4 | 2 | 1 | 62.8 | −3.2 |
| 1,4,5,8-Tetramethylnapthalene | 82 | 4 | 1 | 4 | 0 | 2 | 79.1 | 2.9 |
| 1,2,4,7-Tetramethylnapthalene | 25.15 | 4 | 1 | 4 | 1 | 0 | 26.7 | −1.6 |
| 1,3,6,8-Tetramethylnapthalene | 43.35 | 4 | 1 | 4 | 0 | 1 | 47.6 | −4.2 |

**Table 4c**
Group additivity results for the 5-8 methyl substituted naphthalenes. All $\Delta H_f{}^{\circ}{}_{298}$ values in kJ mol$^{-1}$.

| Name | $\Delta H_f{}^{\circ}{}_{298}$ calc (G3MP2) | Methyl | Nap | BOND | CO | PERI | $\Delta H_f{}^{\circ}{}_{298}$ calc (GA) | $\Delta$ ($\Delta H_f{}^{\circ}{}_{298}$) |
|---|---|---|---|---|---|---|---|---|
| 1,2,3,4,6-Pentamethylnapthalene | 17.27 | 5 | 1 | 5 | 4 | 0 | 14.5 | 2.8 |
| 1,2,3,4,5-Pentamethylnapthalene | 47.64 | 5 | 1 | 5 | 4 | 1 | 44.5 | 3.2 |
| 1,2,3,5,7-Pentamethylnapthalene | -0.53 | 5 | 1 | 5 | 2 | 0 | 0.7 | −1.2 |
| 1,2,3,6,7-Pentamethylnapthalene | -1.27 | 5 | 1 | 5 | 2 | 0 | 0.6 | −1.8 |
| 1,2,3,5,6-Pentamethylnapthalene | 6.46 | 5 | 1 | 5 | 3 | 0 | 8.3 | −1.8 |
| 1,2,4,6,7-Pentamethylnapthalene | -6.79 | 5 | 1 | 5 | 1 | 0 | −5.5 | −1.3 |
| 1,2,4,6,8-Pentamethylnapthalene | 20.83 | 5 | 1 | 5 | 1 | 1 | 23.1 | −2.2 |
| 1,2,3,5,8-Pentamethylnapthalene | 29.24 | 5 | 1 | 5 | 2 | 1 | 33.8 | −4.5 |
| 1,2,4,5,6-Pentamethylnapthalene | 30.42 | 5 | 1 | 5 | 2 | 1 | 23.0 | 7.5 |
| 1,2,4,5,8-Pentamethylnapthalene | 57.12 | 5 | 1 | 5 | 1 | 2 | 53.1 | 4.1 |
| 1,2,3,6,8-Pentamethylnapthalene | 27.24 | 5 | 1 | 5 | 2 | 1 | 29.1 | −1.9 |
| 1,2,3,7,8-Pentamethylnapthalene | 33.9 | 5 | 1 | 5 | 3 | 1 | 36.7 | −2.8 |
| 1,2,4,5,7-Pentamethylnapthalene | 20.59 | 5 | 1 | 5 | 1 | 1 | 23.1 | −2.5 |
| 1,2,4,7,8-Pentalmethylnapthalene | 31.61 | 5 | 1 | 5 | 2 | 1 | 30.7 | 0.9 |
| 1,2,3,4,5,6-Hexamethylnapthalene | 19.71 | 6 | 1 | 6 | 5 | 1 | 18.4 | 1.3 |
| 1,2,3,4,5,7-Hexamethylnapthalene | 13.68 | 6 | 1 | 6 | 4 | 1 | 10.8 | 2.9 |
| 1,2,3,4,6,7-Hexamethylnapthalene | -15.67 | 6 | 1 | 6 | 4 | 0 | −17.8 | 2.1 |
| 1,2,3,5,6,7-Hexamethylnapthalene | -20.16 | 6 | 1 | 6 | 4 | 0 | −17.8 | −2.4 |
| 1,2,3,5,6,8-Hexamethylnapthalene | 3.92 | 6 | 1 | 6 | 3 | 1 | 4.6 | −0.7 |
| 1,2,3,5,7,8-Hexamethylnapthalene | 2.64 | 6 | 1 | 6 | 3 | 1 | 4.6 | −2.0 |
| 1,2,3,6,7,8-Hexamethylnapthalene | 5.21 | 6 | 1 | 6 | 4 | 1 | 10.7 | −5.5 |
| 1,2,3,4,5,8-Hexamethylnapthalene | 44.38 | 6 | 1 | 6 | 4 | 2 | 40.8 | 3.6 |
| 1,2,4,5,6,8-Hexamethylnapthalene | 30.68 | 6 | 1 | 6 | 2 | 2 | 27.0 | 3.7 |
| 1,2,4,5,7,8-Hexamethylnapthalene | 27.55 | 6 | 1 | 6 | 2 | 2 | 27.0 | 0.5 |
| 1,2,3,4,5,6,8-Heptamethylnapthalene | 14.64 | 7 | 1 | 7 | 5 | 2 | 14.8 | −0.1 |
| 1,2,3,4,5,6,7-Heptamethylnapthalene | −9.1 | 7 | 1 | 7 | 6 | 1 | −15.3 | 6.2 |
| 1,2,3,4,5,6,7,8-Octamethylnapthalene | −2.07 | 8 | 1 | 8 | 8 | 2 | 2.5 | −4.6 |

additivity method uses the base value of the aromatic compound (benzene or naphthalene) and three parameters: the $CH_3$–$CH_2$ bond (BOND), constrained "ortho" (CO), and the "peri" (PERI) interactions. These interactions are per bonding group, in this case the methyl group, and are depicted in Fig. 1. These parameter values were determined by enumerating the groups and group interactions in each molecule and then using a least-squares fit to minimize the difference between the calculated (G3MP2 and B3PW91) values and the values obtained by using the group additivity interaction parameters. This is the same method originally outlined by Benson and further refined by Whiteside, Joback, and Gronert, among others [5,6,20,21]. The values of these parameters are presented in Table 3. It is worth noting that the average difference between the parameter values obtained by G3MP2 versus B3PW91 is 2.3 kJ mol$^{-1}$. This implies that while the parameters obtained by the G3MP2 values are the most accurate, the cheaper DFT method may also be used to determine these parameters values, with only a small loss in accuracy. However, the reader should be cautioned that since the parameters are additive, as the number of times each is used increases, the difference between the parameters will increase as well.

The enumeration and calculation of the substituted benzene and naphthalene compounds are presented in Tables 4a–4c using the G3MP2 calculated values. The group additivity method worked well for these compounds, with the twelve substituted benzene compounds having a RMS value of 1.8 kJ mol$^{-1}$ and the seventy-five substituted naphthalene compounds having a RMS value of 2.1 kJ mol$^{-1}$ when compared to the G3MP2 values.

## 4. Conclusions

This work calculated the enthalpy of formation for all of the methyl substituted naphthalene compounds using multiple levels of theory. The highest level calculation (G3MP2) agreed well with all of the experimentally determined values, although it is computationally expensive. The differences between calculated values vary greatly between the different computational methods.

A group-additivity model was developed by determining the intra-molecular interactions and, based on the results of the G3MP2 and B3PW91 calculations, assigned values. These values were compared and found to differ by 2.3 kJ mol$^{-1}$. This implies that while DFT calculations on a single molecule may be inaccurate, by coupling these calculations with a group additivity method, and using a large collection of molecules, these inaccuracies may be mitigated and useful results obtained. The group additivity method produces acceptable results; however, it is an inflexible model, and without the appropriate experimental (or calculated) values, it cannot be extensively or accurately developed. For these reasons, it may be more appropriate to carry out the high-level calculations versus developing a group-additivity model for complex molecules.

In future work, we plan to continue this series of calculations to methyl substituted phenanthrene, pyrene, and other aromatic compounds. This will allow us to determine other interactions and verify that the interactions are consistent between types of molecules using the group-additivity model as well as compare the calculated results to the experimental values.

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