A Calorimetric Study of *peri* Strain in 1,8-Dimethylnaphthalene and 1,4,5,8-Tetramethylnaphthalene

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Enthalpies of combustion, utilizing a micro combustion calorimetric technique, and enthalpies of sublimation have been determined for 1,8-dimethylnaphthalene and 1,4,5,8-tetramethylnaphthalene. Standard enthalpies of formation for the compounds in the gaseous state, $\Delta H_f^\circ (g)$, have been derived and are $(26.0 \pm 0.7)$ and $(19.5 \pm 0.9)$ kcal mol$^{-1}$, respectively. The calculated strain energies caused by *peri* interactions in the two compounds are 6 and 15 kcal mol$^{-1}$, respectively.

Substitution in the 1,8-positions in naphthalene is generally referred to as *peri* substitution. Due to the structure of the naphthalene molecule such substituents come closer together than if they were *ortho*. As was pointed out in the review by Balasubramaniamy *peri* interactions in naphthalene early aroused considerable interest among chemists, an interest that seems to be increasing rather than decreasing.

Thermochemical methods have not been utilized in the study of *peri* interactions in true naphthalene derivatives until quite recently. In two independent investigations, the energy of combustion was determined for crystalline 1,8-dimethylnaphthalene. In Ref. 2 energies of combustion were also reported for the 2,3-, 2,6-, and 2,7-isomers. From these measurements enthalpies of formation for the compounds in the crystalline state are derived. However, in studies of intramolecular interactions gas phase enthalpies of formation generally are those that contain the pertinent information. Enthalpy of vaporization (sublimation) determinations therefore are an essential part of such investigations. The development of a micro-bomb (4.3 cm$^3$) combustion calorimeter now makes it possible to perform a full series of combustion measurements on 50 mg or less of pure material, yet with adequate accuracy. Calorimetric enthalpy of vaporization measurements for compounds with vapour pressures at 298 K extending down into the $10^{-4}$ Torr* region in most cases have become a routine procedure in our laboratory.

In this paper enthalpy of combustion and sublimation measurements are reported for 1,8-dimethylnaphthalene (1,8-DMN) and 1,4,5,8-tetramethylnaphthalene (1,4,5,8-TMN). One of the questions asked was whether the first pair of *peri* methyl groups in the 1,8-DMN molecule would make it more "costly", or perhaps less so, to introduce the second *peri* pair in the 4,5-positions. Or, would the stepwise *peri* dimethyl substitutions in naphthalene cause constant increments in the energy?

The so called *ortho*-effect for a pair of methyl groups in benzene has been investigated previously by combustion calorimetry, in combination with calorimetric measurements of enthalpies of vaporization. The calculated mean value for the strain energy introduced by two *ortho* methyl groups is of the order of 0.6 - 0.7 kcal mol$^{-1}$. The magnitude of the expected increased strain due to the much closer proximity of *peri* methyl groups should be an interesting piece of information derivable from the calorimetric measurements.

EXPERIMENTAL

Compounds. The benzoic acid used in the calibration experiments was National Bureau of Standards SRM 391.

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* 1 Torr = (101.325/760) kPa.
** 1 cal = 4.184 J.
The 1,8-dimethylnaphthalene (DMN) sample has been accounted for earlier.\textsuperscript{1} 1,4,5,8-Tetramethylnaphthalene (TMN) was synthesized by Dr. Hans Sternrup (Department of Organic Chemistry, Chemical Center, Lund) from p-xylene and \(\gamma\)-valerolactone as described in Ref. 8. About 2.5\% of impurities remained after two recrystallizations from methanol. Running the material through a neutral aluminum oxide column, with pentane as eluent, did not markedly improve the purity. Subsequent recrystallization (twice) from hexane reduced the total amount of GLC detectable impurity to 0.13 mol\%. Carbowax and silicone (SE-30) columns were used in the GLC studies. Mass spectrometric analysis, coupled with GLC, identified the impurities as an isomeric tetramethyl- and a trimethyl-naphthalene, present in approximately equal amounts. The NMR spectrum was fully consistent with the assumed 1,4,5,8-arrangement of the four methyl groups. The purified material was pressed into a pellet, which was then broken up and ground in an agate mortar to ascertain the escape of traces of solvent (hexane) that might be trapped in the crystalline material.\textsuperscript{*} The melting temperature, determined on a Perkin-Elmer DSC-2 differential scanning calorimeter was 405.\textsuperscript{±} K. For the combustion measurements 3.5 mm diameter pellets were made. The mass loss from such a pellet was less than 1\,\mu{g}\textper

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to determine enthalpies of fusion. High purity indium was used as calibration standard and naphthalene was included in the series for comparison. The enthalpies of fusion obtained for naphthalene, DMN, and TMN were 18.8, 15.8, and 23.9\,kJ mol\textsuperscript{−1}, respectively. McCullough et al.\textsuperscript{16} obtained 18.98\,kJ mol\textsuperscript{−1} for naphthalene.

**Combustion calorimetry.** The micro combustion calorimeter as well as the calorimetric procedure were identical to those described in Ref. 3. Details of the combustion measurements on DMN have already been given together with the resulting standard energy of combustion for the crystalline material.\textsuperscript{1} In the combustion experiments on TMN the initial pressure of oxygen, \(P\,\text{(O}_2\text{)}\), varied around 35 atm;\textsuperscript{*} for DMN it was 31 atm. Five experiments were performed on TMN; in one a small correction for unburned carbon had to be applied. The energy equivalent of the calorimetric system was determined by combustion of benzaldehyde; series III in Ref. 3. The constancy of the calibration was checked by performing electrical calibrations in three of the runs on TMN; (for an account of the agreement between benzoic acid and electrical calibrations cf. Ref. 3).

All weighings of sample were made on a Mettler M5 micro balance, which had been carefully calibrated against standard weights,\textsuperscript{4} calibrated at the National Bureau of Standards.

The weighings have been reduced to masses and molar masses computed from the 1969 table of atomic weights.\textsuperscript{11} The corrections to standard states, \(\Delta U_c\), were calculated using a computer program based on the procedure by Hubbard et al.\textsuperscript{18} The estimated values for \(c_p\) and \(\left(\partial H/\partial T\right)_p\) were the same as those in Ref. 3. The final overall precision of the \(\Delta U_c\) mean values was estimated as recommended by Rossini.\textsuperscript{13} The reference temperature of the combustion experiments is 298.15 K.

**Vaporization calorimetry.** The enthalpies of sublimation at 298.15 K were measured using the Morawetz calorimeter.\textsuperscript{4} Five determinations were made on DMN following the procedure described in Ref. 4, with around 13 mg evaporated per experiment.

Heating the vaporization calorimeter to temperatures above \(\sim 335\,\text{K}\) was not considered “safe” and TMN therefore could not be melted directly into the evaporation pan. Furthermore, the compound could only be sublimed into the calorimeter at a very slow rate. Instead TMN was melted into a thin-walled gold cup that was then “soldered” to the evaporation chamber with gallium. Four test experiments on octadecane yielded (153.6 ± 1.1)\,kJ mol\textsuperscript{−1} (mean and standard deviation of the mean); literature values are 153.1\textsuperscript{14} and 152.7\textsuperscript{18}\,kJ mol\textsuperscript{−1}. When three successful vaporization experiments had been performed on TMN the calorimeter as such failed and further measurements had to be postponed. The sublimation enthalpy reported here is the mean value from these three determinations. Around 2.5\,mg of TMN had evaporated per experiment. In the evaluation of the overall uncertainty of the enthalpy of sublimation for TMN, the standard deviation of the measured mean value, 0.40\,kJ mol\textsuperscript{−1}, was raised to 0.60\,kJ mol\textsuperscript{−1} to allow for a possible systematic error in this particular series of measurements.

**RESULTS AND DISCUSSION**

The results from the combustion experiments on TMN are given in Table 1, with \(\Delta U_c\) referring to unit mass of sample. For DMN the corresponding mean value and standard deviation of the mean is \(\Delta U_0\,(\text{DMN}) = (41323 \pm 5)\,\text{J g}^{-1}\). The \(\Delta U_c\) values refer to the idealized combustion reaction in which all reactants and products are in their thermodynamic standard states at 298.15 K. Table 2 gives the standard molar energies, \(\Delta U_c\), and enthalpies, \(\Delta H_c\), of combustion for the compounds in the crystalline state at 298.15 K. Also listed in Table 2 are the molar enthalpies of sublimation, \(\Delta H_{\text{subL}}\) and derived enthalpies of formation, \(\Delta H_f\), for the compounds in the crystalline and gaseous states (298.15 K). The enthalpies of formation at
Table 1. Energy of combustion measurements at 298.15 K of 1,4,5,8-tetramethylnaphthalene. 
\( \varepsilon(\text{calor}) = (583.45 \pm 0.07) \text{ J K}^{-1} \). For explanation of symbols, cf. Ref. 12.

<table>
<thead>
<tr>
<th>( m'/\text{mg} )</th>
<th>8.023</th>
<th>8.426</th>
<th>8.282</th>
<th>7.923</th>
<th>7.893</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon(\text{cont})/\text{J K}^{-1} )</td>
<td>0.261</td>
<td>0.261</td>
<td>0.263</td>
<td>0.262</td>
<td>0.262</td>
</tr>
<tr>
<td>( \Delta H/K )</td>
<td>0.58016</td>
<td>0.60908</td>
<td>0.59876</td>
<td>0.57277</td>
<td>0.57046</td>
</tr>
<tr>
<td>( \Delta U_{\text{rig}}/J )</td>
<td>0.239</td>
<td>0.236</td>
<td>0.255</td>
<td>0.237</td>
<td>0.159</td>
</tr>
<tr>
<td>( \Delta U(\text{C})/J^* )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.188</td>
<td>0</td>
</tr>
<tr>
<td>( -\Delta U_{\text{c}}(\text{comp})/J \text{ mg}^{-1} )</td>
<td>42.156</td>
<td>42.142</td>
<td>42.146</td>
<td>42.170</td>
<td>42.143</td>
</tr>
</tbody>
</table>

Mean and std. dev. of the mean: \( \Delta u_c^\circ = -(42151 \pm 5) \text{ J g}^{-1} \)

* Correction for unburned carbon: 0.033 J \( \mu \text{g}^{-1} \).

Table 2. Results and derived quantities at 298.15 K. The uncertainties given are twice the final overall standard deviation of the mean. 1 cal = 4.184 J.

<table>
<thead>
<tr>
<th>1,8-Dimethyl-naphthalene</th>
<th>1,4,5,8-Tetramethylnaphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta U_c^\circ/\text{kJ mol}^{-1} )</td>
<td>-6455.8 \pm 2.6</td>
</tr>
<tr>
<td>( \Delta H_c^\circ/\text{kJ mol}^{-1} )</td>
<td>-6463.2 \pm 2.6</td>
</tr>
<tr>
<td>( \Delta H_f^\circ(\text{c})/\text{kJ mol}^{-1} )</td>
<td>26.1 \pm 3.0</td>
</tr>
<tr>
<td>( \Delta H_f^\circ(\text{cal})/\text{kJ mol}^{-1} )</td>
<td>82.7 \pm 0.3</td>
</tr>
<tr>
<td>( \Delta H_f^\circ(g)/\text{kJ mol}^{-1} )</td>
<td>108.8 \pm 3.0</td>
</tr>
<tr>
<td>( \Delta H_f^\circ(g)/\text{kcal mol}^{-1} )</td>
<td>26.0 \pm 0.7 ( _s )</td>
</tr>
</tbody>
</table>

298.15 K for gaseous carbon dioxide and liquid water used in the calculations are from Ref. 16.

The selected standard enthalpy of formation for gaseous naphthalene \( ^7 \) becomes 35.9 \pm 0.2 kcal mol\(^{-1} \)* when two recent determinations of its enthalpy of sublimation \( ^18,19 \) are taken into account. In the series naphthalene, 1,8-DMN, 1,4,5,8-TMN the increments in the gaseous enthalpies of formation are \(-(10.0 \pm 0.7)\) and \(-(6.5 \pm 1.0)\) kcal mol\(^{-1}\), respectively.** This means that the di-peri substitution causes a strain that is 3.4 kcal mol\(^{-1}\) larger than what might have been predicted on the basis of results for the mono-peri compound alone. Since the structures of these particular compounds are not yet known this result cannot be rationalized in terms of, e.g., molecular deformations.

The absolute values of the strain introduced by the methyl-methyl peri interactions can be evaluated in a number of more or less equivalent ways. For instance, the average increment in the gas phase standard enthalpy of formation for methyl substitution in the series benzene, toluene, \( m \)-xylene, 1,3,5-trimethylbenzene \( ^5-7 \) is equal to \(-7.87\) kcal mol\(^{-1}\). This increment, combined with the enthalpy of formation of naphthalene, can be used to calculate enthalpies of formation for unstrained di- and tetramethylnaphthalenes. The values obtained are 20.2, and 4.3 kcal mol\(^{-1}\), respectively, implying that the peri strain in 1,8-DMN is 5.3, kcal mol\(^{-1}\), whereas it amounts to as much as 15.4 kcal mol\(^{-1}\) in 1,4,5,8-TMN.

The enthalpy change for the isomerization reaction

\[
\begin{align*}
\text{2} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\rightarrow
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

is a direct measure of the strain in 1,8-DMN, since 1-methylnaphthalene as well as naphthalene in this context are to be considered as

\( ^* \) To facilitate comparisons with other results in the literature the discussion of the final results will be in terms of calories rather than the SI unit Joule.

** Unless otherwise stated the uncertainties are twice the final overall standard deviation of the mean. The enthalpy of formation differences can be calculated almost directly from the differences in combustion and vaporization enthalpies and therefore the overall uncertainties in these quantities were used in such calculations.

unstrained.* The peri strain energy calculated in this way is \((6.4 \pm 1.4)\) kcal mol\(^{-1}\). The similarly calculated peri strain in 1,4,5,8-TMN is \((15.4 \pm 2.3)\) kcal mol\(^{-1}\).

* Added in proof. A recent study of the crystal structure of 1,8-DMN by D. Bright, I. E. Maxwell and J. de Boer (J. Chem. Soc. Perkin Trans. 2 (1973) 2101), in connection with strain energy minimization calculations, shows that the repulsive interaction between the peri methyl groups is reduced mainly by bond-angle distortion at the junction between the methyl groups and the naphthalene nucleus. The inner angles are increased from the ideal 120° to almost 125°. The naphthalene skeleton, however, remains planar and there is no detectable out-of-plane displacement of the methyl groups. These are found to be in the fixed orientation, where four of the methyl hydrogens face each other in pairs, and the remaining two practically lie in the plane of the aromatic rings.

The peri 4,5-hydrogens are found to be bent towards one another, such that the distance between them is reduced to 2.17 Å (from 2.43 Å). The results from the strain energy minimization calculations are in good agreement with the observed molecular geometry, except that they do not reproduce the "bending" of the peri 4,5-hydrogens.

Considering the general features of the 1,8-DMN structure, it seems reasonable that the second peri dimethyl substitution should be more costly than the first, in agreement with the calorimetric studies. A comparison between the numerical values of the minimization-calculated and the thermochemically derived strain energies is not meaningful, since the reference systems are not directly comparable.

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REFERENCES


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