Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 3,7-diamino-2,4,6,8-tetranitro-1,5-diazenaphthalene (DATNP) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazenaphthalene 1,5-N-oxide (DATNPO)

by Edward FC Byrd
NOTICES

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Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 3,7-diamino-2,4,6,8-tetranitro-1,5-diazaanaphthalene (DATNP) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazaanaphthalene 1,5-N-oxide (DATNPO)

by Edward FC Byrd

Weapons and Materials Research Directorate, ARL
Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene (DATNP) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide (DATNPO)

The US Army Research Laboratory–developed series of scripts, written to dramatically simplify the computation of crystalline density and heat of formation, were used to evaluate the performance properties for the 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene (DATNP) (1) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide (DATNPO) (2) notional energetic materials. Additionally, a qualitative estimation of the impact sensitivities has been calculated. This report outlines the procedures used to generate this information, as well as Cheetah calculations using the predicted crystalline density and heat of formation.
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**Acknowledgments**

Dr Betsy Rice and Jennifer J Hare are acknowledged for their efforts in the original coding of the neutral heat of formation and EDAT tools, respectively. Dr Anthony Yau is acknowledged for his work in revising the EDAT code. Dr James Ianni (Applications Engineer with Lockheed-Martin, contractor to the US Army Research Laboratory Department of Defense [DOD] Supercomputing Resource Center [ARL DSRC]) is acknowledged for his “gsSubmit” script, initially written for the ARL DSRC. Dr Betsy Rice is acknowledged for running the Cheetah calculations. All computations were performed at the ARL DSRC, Aberdeen Proving Ground, MD. Calculations were performed at the behest of Dr Gary K Windler (Los Alamos National Laboratory).
1. **Introduction**

US Army Research Laboratory (ARL) researchers have achieved robust theoretical models capable of predicting performance properties, such as heats of formation,\textsuperscript{1,2} densities,\textsuperscript{3,4} and impact sensitivity\textsuperscript{5} of energetic materials, and have begun growing advanced synthesis capabilities to realize notional materials. This dual capability allows synthetic and formulation chemists to safely and quickly screen candidate materials to focus efforts only on the most promising compounds. For an in-depth explanation of the different theoretical methods employed herein, please refer to previous works.\textsuperscript{6,7} This technical note will detail theoretical predictions of heat of formation, density, sensitivity, and performance for the 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene (DATNP) (1) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide (DATNPO) (2).\textsuperscript{8}

2. **Results and Discussion**

The properties of 1 and 2 (Figs. 1a–b) were predicted using the ARL-developed scripts described in more detail in a previous report.\textsuperscript{7} For the estimation of the impact sensitivities, the electrostatic maps on the 0.001 isosurfaces were generated with the scalar range of the electrostatic surface potential (ESP) ranging from –0.05 to 0.075. Recall that for this visualization methodology, regions of large positive charge (i.e., electron deficient regions, labeled as red) over the backbone of the structure tend to indicate increased sensitivity.
The computed heats of formation and crystalline densities for these molecules are presented in Table 1.

Table 1  Computed heats of formation and crystalline densities for 1 and 2

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Solid phase heat of formation (kcal/mol)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.899</td>
<td>1.863</td>
</tr>
<tr>
<td>2</td>
<td>46.903</td>
<td>1.932</td>
</tr>
</tbody>
</table>

Additionally, we plot the ESP maps for 1 (Figs. 2a–b) and 2 (Figs. 3a–b) with and without the molecule overlaid on the ESP. When the images are analyzed, we would quantify both molecules as slightly sensitive to insensitive. We performed Cheetah 8.0 calculations⁹ to predict the performance parameters using the predicted heats of formation and densities. At the Chapman-Jouguet point, Cheetah yields the values shown in Table 2.
Fig. 2  Electrostatic potential map of 1, without a) and with b) molecule overlay

Fig. 3  Electrostatic potential map of 2, without a) and with b) molecule overlay

<table>
<thead>
<tr>
<th>Table 2  Cheetah predicted properties for 1 and 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
</tbody>
</table>

Note: TNT = trinitrotoluene
3. Conclusions

The ARL-developed software tools were used to predict the heats of formation and crystalline densities of the 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene (DATNP) (1) and 3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide (DATNPO) (2) molecules. Using this predicted data, we then ran Cheetah calculations to predict the performance of these materials. Additionally, we predicted the qualitative impact sensitivities of these compounds using electrostatic potential maps. This information has been transitioned back to the requesting synthetic chemist, Dr Gary K Windler of Los Alamos National Laboratory.
4. References


## List of Symbols, Abbreviations, and Acronyms

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARL</td>
<td>US Army Research Laboratory</td>
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<tr>
<td>cm³</td>
<td>grams per cubic centimeter</td>
</tr>
<tr>
<td>DATNP</td>
<td>3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene</td>
</tr>
<tr>
<td>DATNPO</td>
<td>3,7-diamino-2,4,6,8-tetranitro-1,5-diazanaphthalene 1,5-N-oxide</td>
</tr>
<tr>
<td>DSRC</td>
<td>Department of Defense (DOD) Supercomputing Resource Center</td>
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<tr>
<td>ESP</td>
<td>electrostatic surface potential</td>
</tr>
<tr>
<td>kcal/mol</td>
<td>kilocalories per mole (unit of energy)</td>
</tr>
<tr>
<td>TNT</td>
<td>trinitrotoluene</td>
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</table>
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