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US Army Research Laboratory

Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo (3:3:0)octan-2-one

by Edward FC Byrd

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14. ABSTRACT
Using the US Army Research Laboratory–developed series of scripts, written to dramatically simplify the computation of crystalline density and heat of formation, the performance properties for the 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo(3:3:0)octan-2-one notional energetic material were evaluated. Additionally, a qualitative estimation of the impact sensitivity 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.

15. SUBJECT TERMS
computational toolbox, script, crystalline density, heat of formation, impact sensitivity, energetic materials

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[1] Chaykovsky M, Koppes WM, inventors; The United States of America as represented by the Secretary of the Navy, assignee. 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo[3:3:0]octan-2-one. United States patent US 5,262,544. 1993 Nov 16.

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1. Introduction

US Army Research Laboratory (ARL) researchers have achieved robust theoretical models capable of predicting performance properties, such as heats of formation,[1,2] densities,[3,4] and impact sensitivity[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.[6,7] This technical note will detail theoretical predictions of heat of formation, density, sensitivity, and performance for the 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo(3:3:0)octan-2-one molecule.[8]

2. Results and Discussion

The properties of the 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo(3:3:0)octan-2-one molecule (Fig. 1) were predicted using the ARL tools.[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.

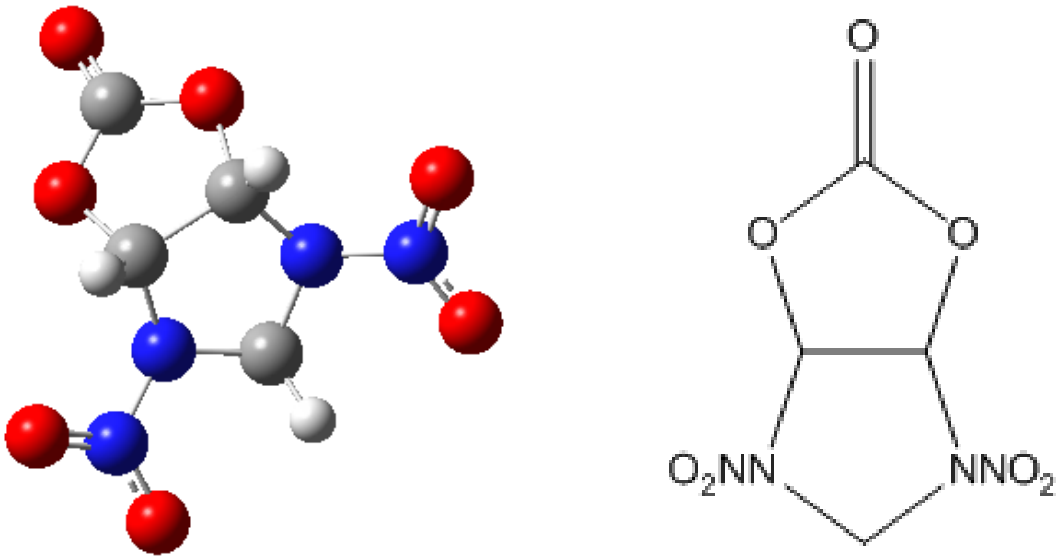

Fig. 1 Optimized structure of the 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo(3:3:0)octan-2-one molecule

The computed gas and solid heats of formation using the group additivity method were –82.11 and –106.43 kcal/mol, respectively. The predicted crystalline density was 1.888 g/cm^3. The experimental density for this compound is known (1.952 g/cm^3), resulting in a –3.3% error, on par with the published root mean square error of approximately 3%.[4]

Additionally, we plot the ESP maps for this molecule (Fig. 2a–c), with and without the molecule overlaid on the ESP. When the images are analyzed, we would quantify the molecule as marginally sensitive, with the large red section being somewhat misleading as it is due to the presence of hydrogens and not the backbone structure. The experimental h_{50} impact sensitivity for this compound is 59 cm (with a reference cyclotrimethylenetrinitramine [RDX] sensitivity of 19 cm). We performed Cheetah 8.0 calculations[9] to predict the performance parameters using the predicted heat of formation and density. At the Chapman-Jouguet point, Cheetah yields the values shown in Table 1. When the experimental density and the predicted heat of formation are used, Cheetah yields the values shown in Table 2.

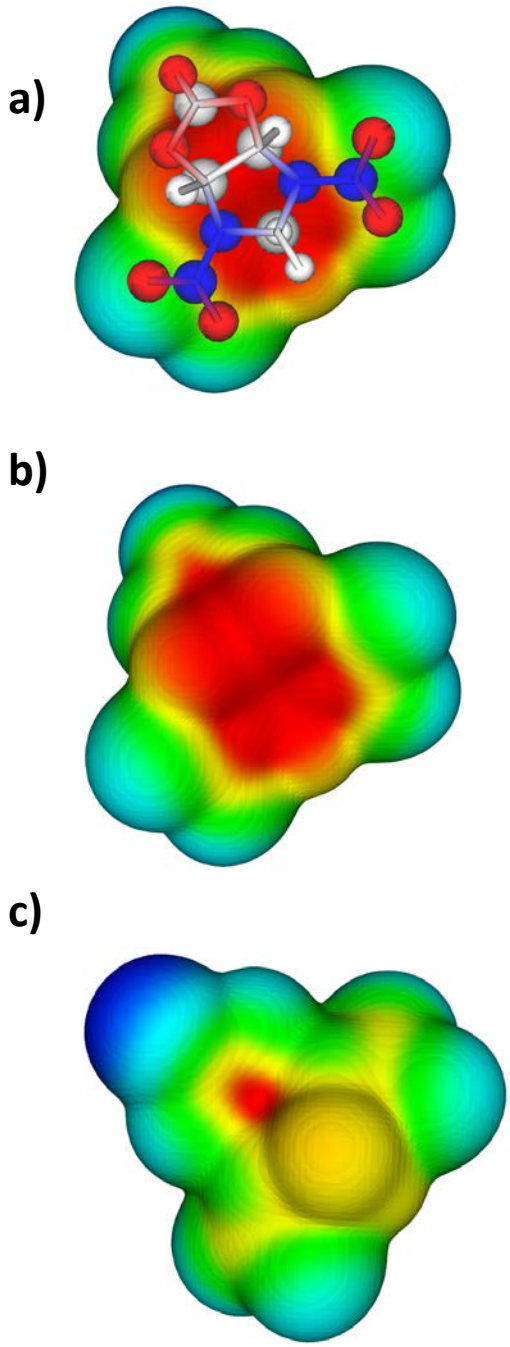

Fig. 2 Electrostatic potential map of 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo(3:3:0)octan-2-one, a) with and b-c) without molecule overlay. Image c) shows the opposite side of the molecule than b).

Table 1 Cheetah predicted properties for 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo(3:3:0)octan-2-one using predicted density (1.888 g/cm^3)

Property	Value
Pressure	29.783 GPa
Shock velocity	8.196 km/s
Temperature	2974.1 K
Total energy of detonation	1.109 TNT equivalence (per cm^3) 0.971 TNT equivalence (per gram)

Note: TNT = trinitrotoluene

Table 2 Cheetah predicted properties for 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo(3:3:0)octan-2-one using experimental density (1.952 g/cm^3)

Property	Value
Pressure	32.491 GPa
Shock velocity	8.454 km/s
Temperature	2876.7 K
Total energy of detonation	1.163 TNT equivalence (per cm^3) 0.986 TNT equivalence (per gram)

3. Conclusions

The ARL-developed software tools were used to predict the heats of formation and crystalline densities of the 5,7-dinitro-5,7-diaza-1,3-dioxabicyclo(3:3:0)octan-2-one molecule. Using this predicted data, we then ran Cheetah calculations to predict the performance of this material. Additionally, we predicted the qualitative impact sensitivity of this compound using electrostatic potential maps. This information has been transitioned back to the requesting synthetic chemist, Dr David Caruana of Naval Surface Warfare Center – Indian Head.

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List of Symbols, Abbreviations, and Acronyms

ARL	US Army Research Laboratory
g/cm^3	grams per cubic centimeter
DSRC	Department of Defense (DOD) Supercomputing Resource Center
ESP	electrostatic surface potential
kcal/mol	kilocalories per mole (unit of energy)
RDX	cyclotrimethylenetrinitramine
TNT	trinitrotoluene

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