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US Army Research Laboratory

Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate (AMDNNM), bis-aminofurazan diamino-octanitro-azobenzene (BAFDAONAB), and bis-nitrofurazan diamino-octanitro-azobenzene (BNFDAONAB)

by Edward FC Byrd

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14. ABSTRACT

Using a series of scripts developed by the US Army Research Laboratory, written to dramatically simplify the computation of crystalline density and heat of formation, the performance properties were evaluated for the 2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate (AMDNNM), bis-aminofurazan diamino-octanitro-azobenzene (BAFDAONAB), and bis-nitrofurazan diamino-octanitro-azobenzene (BNFDAONAB) notional energetic materials. A qualitative estimation of the impact sensitivities has also been calculated. This report outlines the procedures used to generate this information and includes 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. Introduction

US Army Research Laboratory (ARL) researchers have achieved robust theoretical models capable of predicting performance properties including 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 2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate (AMDNNM), bis-aminofurazan diamino-octanitro-azobenzene (BAFDAONAB), and bis-nitrofurazan diamino-octanitro-azobenzene (BNFDAONAB) notional energetic materials.[8]

2. Results and Discussion

The properties of AMDNNM, BAFDAONAB, and BNFDAONAB (Figs. 1a–1c) were predicted using ARL tools.[7] To estimate 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. For this visualization methodology, regions of large positive charge (i.e., electron-deficient regions, labeled in red) over the backbone of the structure tend to indicate increased sensitivity.

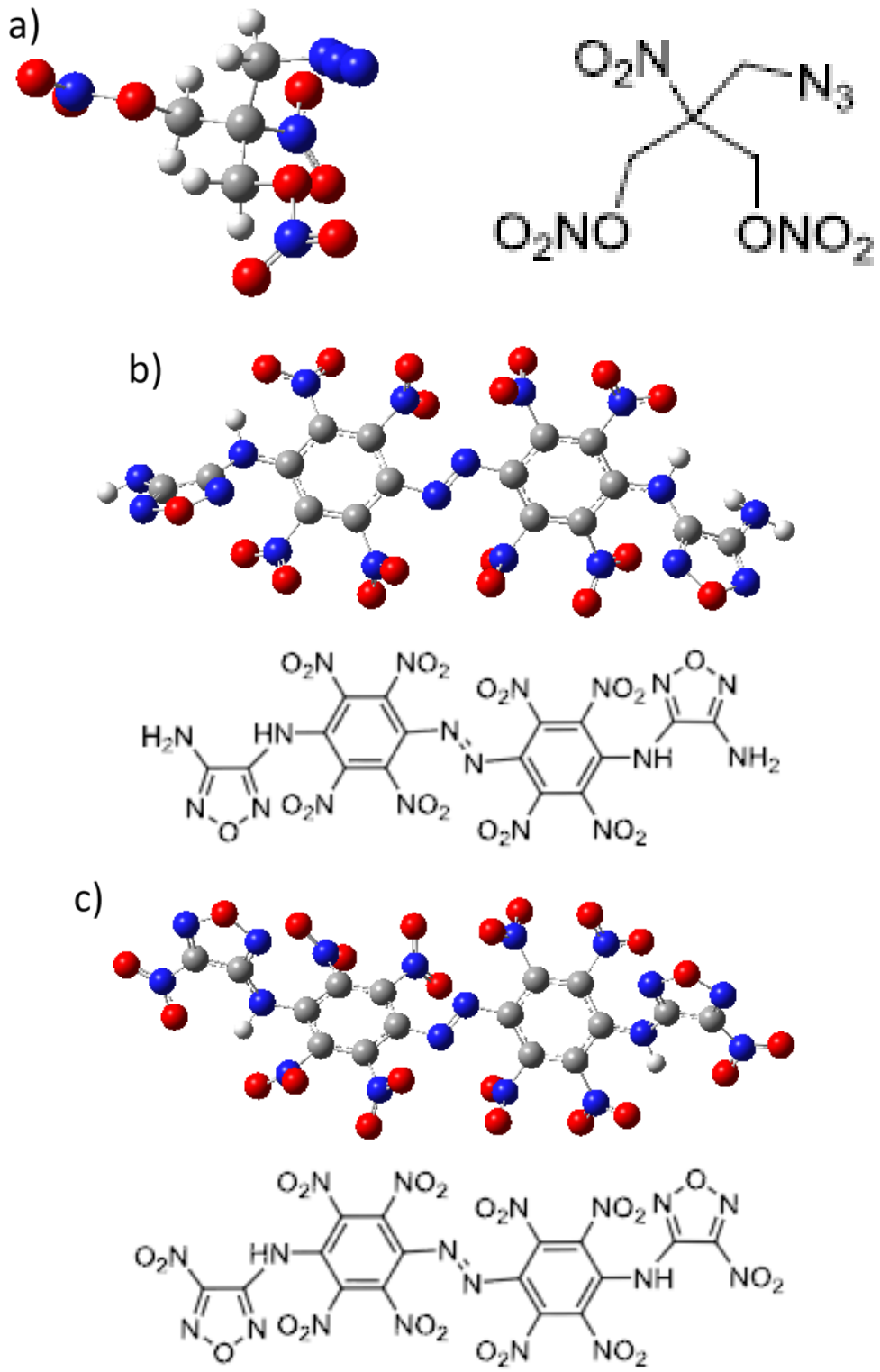

Fig. 1 Optimized structure of a) AMDNNM , b) BAFDAONAB , and c) BNFDAONAB

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 AMDNNM, BAFDAONAB, and BNFDAONAB

Molecule	Solid phase heat of formation (kcal/mol)	Density (g/cm^3)
AMDNNM	1.182	1.720
BAFDAONAB	175.518	1.898
BNFDAONAB	180.912	1.934

Additionally, we plot the ESP maps for AMDNNM (Figs. 2a and 2b), BAFDAONAB (Figs. 3a and 3b), and BNFDAONAB (Figs. 4a and 4b) with and without the molecule overlaid on the ESP. When the images are analyzed, we would quantify AMDNNM as moderately sensitive, BAFDAONAB as slightly sensitive to insensitive, and BNFDAONAB as sensitive. That said, chemist intuition would classify AMDNNM as likely to be very sensitive. It would be of interest to compare the experimental with the predicted results for AMDNNM. We performed Cheetah 8.0 calculations[9] 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.

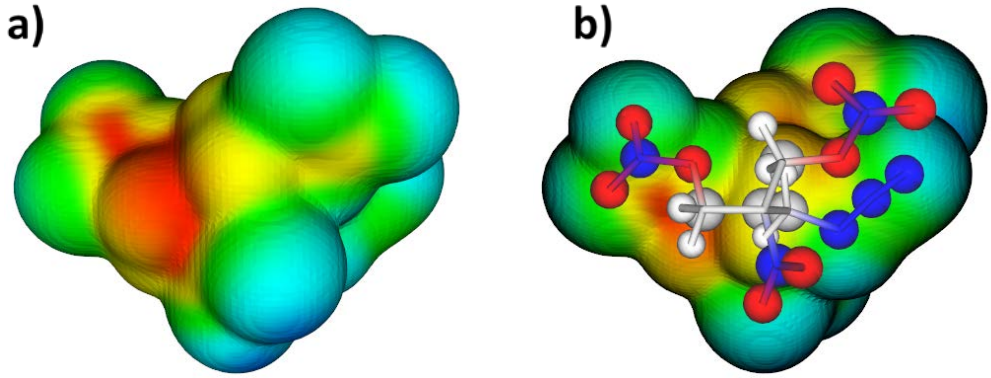

Fig. 2 Electrostatic potential map of AMDNNM: a) without and b) with molecule overlay

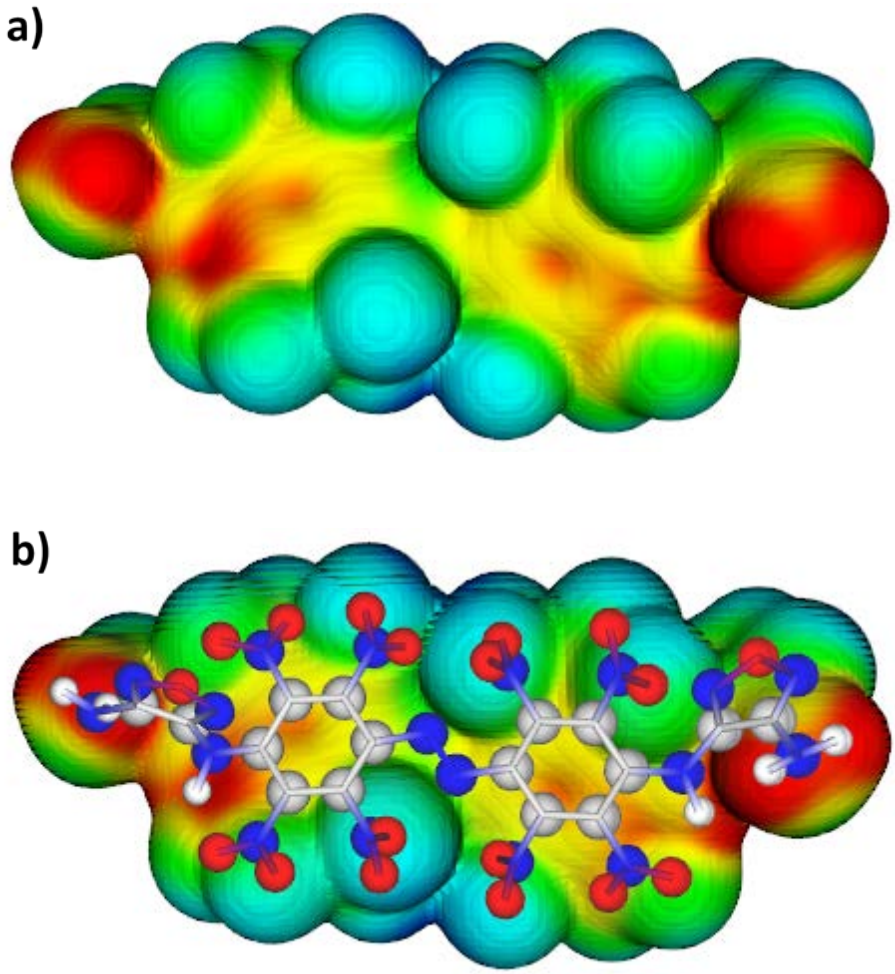

Fig. 3 Electrostatic potential map of BAFDAONAB: a) without and b) with molecule overlay

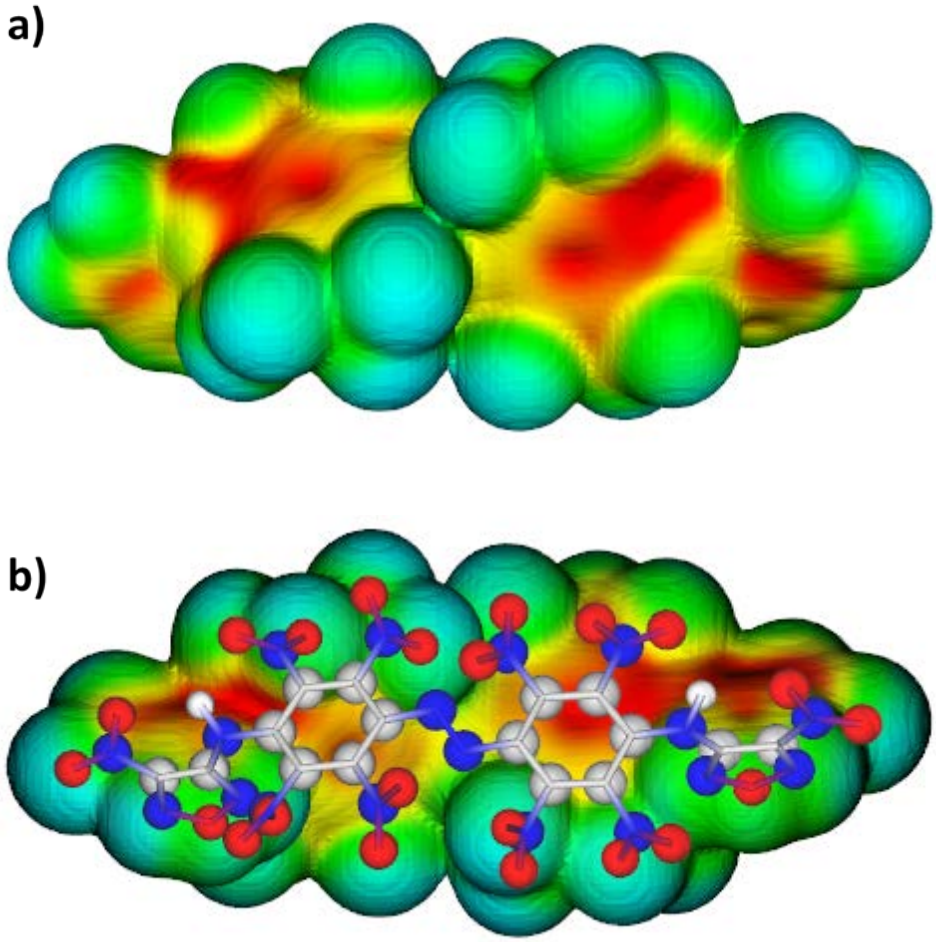

Fig. 4 Electrostatic potential map of BNFDAONAB: a) without and b) with molecule overlay

Table 2 Cheetah-predicted properties for AMDNNM, BAFDAONAB, and BNFDAONAB

Molecule	Pressure (GPa)	Shock velocity (km/s)	Temperature (K)	Total energy of detonation (TNT equivalent) (per cm^3)	Total energy of detonation (TNT equivalent) (per g)
AMDNNM	29.348	8.275	3,663.1	1.349	1.297
BAFDAONAB	31.278	8.545	3,665.6	1.339	1.167
BNFDAONAB	35.442	9.011	4,116.3	1.435	1.227

Note: TNT = trinitrotoluene.

3. Conclusion

The ARL-developed software tools were used to predict the heats of formation and crystalline densities of the AMDNNM, BAFDAONAB, and BNFDAONAB 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 David Boruta of Naval Surface Warfare Center–Indian Head.

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List of Symbols, Abbreviations, and Acronyms

AMDNNM	2-(azidomethyl)-2-nitropropane-1,3-diyl dinitrate
ARL	US Army Research Laboratory
BAFDAONAB	bis-aminofurazan diamino-octanitro-azobenzene
BNFDAONAB	bis-nitrofurazan diamino-octanitro-azobenzene
ESP	electrostatic surface potential
TNT	trinitrotoluene

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