Prediction of Isothermal Equation of State of an Explosive Nitrate Ester by van der Waals Density Functional Theory

4 AUTHORS, INCLUDING:

Aaron Landerville

University of South Florida

30 PUBLICATIONS   **79** CITATIONS

Report Documentation Page		*Form Approved* *OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE **SEP 2009**	2. REPORT TYPE	3. DATES COVERED **00-00-2009 to 00-00-2009**
4. TITLE AND SUBTITLE **Prediction of Isothermal Equation of State of an Explosive Nitrate Ester by van der Waals Density Functional Theory**		5a. CONTRACT NUMBER
		5b. GRANT NUMBER
		5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER
		5e. TASK NUMBER
		5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Research Laboratory,Chemistry Division,Washington,DC,20375**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**

13. SUPPLEMENTARY NOTES

14. ABSTRACT **see report**

15. SUBJECT TERMS

| 16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**3**	

Prediction of Isothermal Equation of State of an Explosive Nitrate Ester by van der Waals Density Functional Theory

Aaron C. Landerville,*,[†] Michael W. Conroy,[†] Ivan I. Oleynik,[†] and Carter T. White[‡]

[†]Department of Physics, University of South Florida, Tampa, Florida 33620 and [‡]Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375

ABSTRACT A new energetic material, nitrate ester 1 (NEST-1), has shown promise as a powerful, technologically attractive explosive. Its physical properties under compression, however, are currently unknown. Accurate density functional calculations together with a reliable empirical van der Waals correction are employed to predict the isothermal hydrostatic equation of state for this material prior to any known experimental results. The accuracy of results obtained from this approach was tested against experimentally known NEST-1 equilibrium properties and found to be excellent.

SECTION Statistical Mechanics, Thermodynamics, Medium Effects
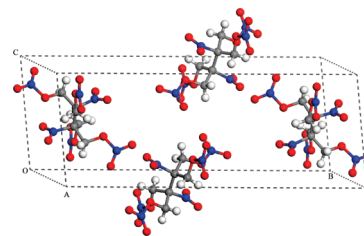
Recently synthesized by Chavez et al.,[1] a novel energetic nitrate ester, 2,3-bis-hydroxymethyl-2,3-dinitro-1,4-butanediol tetranitrate, shows promising properties for use in explosives applications. Herein, this new material will be referred to as NEST-1 (Nitrate ESTer-1), although it has also been termed nitrate ester molecule 1.[1] NEST-1 exhibits sensitivity properties similar to those of pentaerythritol tetranitrate (PETN), and predictions of its performance properties indicate that it is at least as powerful an explosive as cyclotetramethylene tetranitramine (HMX).[1] Importantly, NEST-1 has a relatively low melting point of 85–86 °C as compared to its decomposition point of 141 °C.[1] This means that NEST-1 can be safely melted and cast into a mold, potentially making it useful for a wide variety of applications. Further characterization is required to investigate the potential use of this material.

NEST-1 has a molecular structure similar to that of PETN. However, instead of five carbon atoms, it has six. Two connected carbon atoms constitute the center of the molecule, each bound by one NO_2 group and two CH_2ONO_2 groups, as depicted in Figure 1, giving it the overall chemical formula of $C_6H_8N_6O_{16}$. The NEST-1 crystal has a monoclinic unit cell with $P2_1/n$ symmetry and includes 4 molecules. This structure, combined with its crystal packing, make NEST-1 the most dense nitrate ester yet synthesized, with a density of 1.917 g/cm³.[1]

To explore future applications of NEST-1 as an energetic material, its mechanical and thermodynamical properties are required as an input to engineering modeling. One such fundamental property is its equation of state (EOS). Unfortunately, experimental measurement of the EOS of NEST-1 is costly and currently unavailable. However, it was recently found (see Supporting Information) that properties of energetic materials under compression, such as their equations of state, can be reliably predicted by combining accurate density functional theory (DFT) results with the empirical van der Waals (vdW) correction suggested by Neumann and Perrin[2]
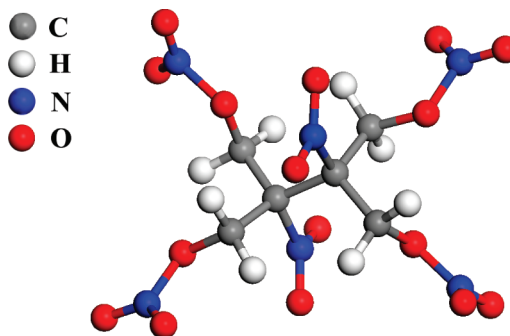
Figure 1. Schematic of a NEST-1 molecule.

for molecular crystals. The vdW term has the form $V_{AB}(r) = d_{AB}(r)C_{6,AB}r^{-6}$, where d_{AB} is a damping function and $C_{6,AB}$ is the coefficient for an empirically fit pairwise interaction between atoms A and B (see ref 2 for additional details).

The Vienna Ab-initio Simulation Package[3,4] was used to perform all DFT calculations using the Perdew–Burke–Ernzerhof functional[5] with projector-augmented wave potentials[6,7] and the Neumann-Perrin vdW correction.[2] Only the gamma point was used to sample the Brillouin zone because of the large unit cell size.[8] The DFT calculations were performed using an energy cutoff of 700 eV and an electronic energy convergence tolerance of 10^{-6} eV, which, when compared with calculations using a range of cutoffs from 400–1000 eV, yielded a convergence better than 0.0015 eV for energy per atom, and 0.015 eV/Å for forces. The conjugate-gradient algorithm was employed to relax all structures until the maximum force on any atom in the unit cell was less than 0.03 eV/Å.

Table 1. Equilibrium Unit-Cell Properties of NEST-1

	a (Å)	b (Å)	c (Å)	α	β	γ	volume (Å^3)
Chavez et al.	8.1228	23.0560	8.5072	90	113.953	90	1456.01
vdW-DFT	8.1894	23.0608	8.5166	90.00	114.449	90.00	1464.18
% diff vdW-DFT	0.82%	0.02%	0.11%	0%	0.44%	0%	0.56%
pure DFT	8.4831	24.0160	8.9550	90.00	115.295	90.00	1649.48
% diff pure DFT	4.44%	4.16%	5.26%	0%	1.18%	0%	13.29%
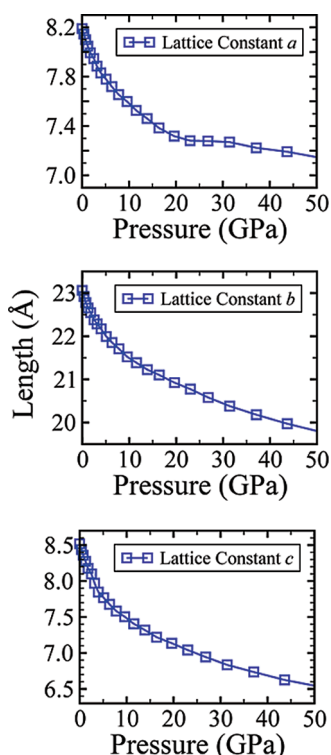
Figure 2. Lattice constants as a function of pressure within the volume compression ratio range of $\eta = V/V_0 = 0.60 - 1.00$. The solid lines are included as guides to the eye.

The experimental structure at ambient conditions was relaxed without constraints to determine the calculated equilibrium structure. Hydrostatic-compression simulations were performed by scaling the volume of the unit cell from 100% to 60% of the calculated equilibrium volume. Relaxations of the unit-cell shape and atomic coordinates were performed at intermediate steps of 2%. The calculated unit-cell properties at equilibrium are displayed and compared with experimental values[1] in Table 1. The agreement of the vdW-DFT calculations with the experimental structure is excellent, yielding an error in unit-cell volume of approximately 0.6%. In contrast, DFT calculations without vdW corrections gave an error in volume of about 13%.

The lattice constants a, b, and c are reported in Figure 2 as a function of pressure. The b and c lattice constants exhibit a relatively smooth monotonic behavior, but the a lattice constant, while still monotonic, first descends more steeply with increasing pressure and then plateaus in the range of 22 to 32 GPa. This plateau occurs over a region where further compression along the a axis is difficult without a rotation and

bending of the nitro groups primarily with respect to the b axis. Completion of this required change, however, is not favored until the pressure reaches around 32 GPa, whereupon compression along the a axis becomes easier. Up to 27 GPa, the computational results for all three lattice constants are well reproduced using fifth-degree polynomials with the fitting coefficients given in Table 2. Although these polynomials provide a compact way of numerically summarizing the computational results up to 27 GPa, they should not be used for greater pressures.

Table 2. Fifth-Degree Polynomial Fits for Pressure Dependence of Lattice Constants and Unit-Cell Volume[a]

| parameter	C_0	C_1 ($\times 10^{-1}$)	C_2 ($\times 10^{-2}$)	C_3 ($\times 10^{-3}$)	C_4 ($\times 10^{-5}$)	C_5 ($\times 10^{-7}$)
a	8.188	−1.276	1.291	−0.883	2.963	−3.663
b	23.023	−3.152	3.064	−2.018	6.868	−9.097
c	8.520	−2.303	2.199	−1.276	3.754	−4.343

[a] Each constant C_n has units of Å/(GPa)^n.

From the hydrostatic compression simulations, the isothermal EOS was obtained and is shown in Figure 3 as a function of the volume compression ratio, $\eta \equiv V/V_0$, where V and V_0 are the compressed and uncompressed volumes, respectively. It is a common practice to fit the EOS data points (either experimental or calculated) by an analytic function of pressure, P, versus η, assuming as parameters the zero pressure isothermal bulk modulus B_0 and its pressure derivative B_0'.[9−11] Such fits can be used to conveniently represent the whole set of numerical data points. In some cases, fitting to an analytic EOS is also used to smooth the experimental data. In addition, if the functional form is physically viable, the analytic EOS obtained from a fit to the data over some lower pressure and compression range can be successfully used to extrapolate the results to higher pressures and compressions. In this work, we fit the vdW-DFT data points using the analytic Birch−Murnaghan EOS,[10]

$$ P = \frac{3}{2} B_0 (\eta^{-7/3} - \eta^{-5/3}) \left[1 + \frac{3}{4} (B_0' - 4)(\eta^{-2/3} - 1) \right] \quad (1) $$

for pressures up to the point closest to 5 GPa, and found that $B_0 = 15.9$ GPa, and $B_0' = 7.1$. Figure 3 shows that this fit yields good agreement with the calculated pressure versus volume data, not only for pressures up to 5 GPa but also throughout the entire range of compressions studied; this range extends up to 44 GPa—well above the Chapman-Jouguet pressure of 40 GPa. Note, however, that care should be exercised when comparing values of B_0 and B_0' obtained from this fit to those obtained from a fit to experimental results when they become

available. One problem is that the values of B_0 and B_0' depend on both the functional form of the EOS assumed[9−11] and the pressure range of the fit. This point, as well as other problems that can arise in the analysis of the experimental and theoretical data, is discussed in detail by Menikoff and Sewell.[12] Moreover, in the case of NEST-1, we have found that increasing B_0 can often be largely compensated by decreasing B_0'. For example, both sets [$B_0 = 15.9$ GPa and $B_0' = 7.1$] and [$B_0 = 17.7$ GPa and $B_0' = 6.4$] provide good fits to the computed data, when used with the analytic Birch−Murnagham EOS, as shown in Figure 3. Therefore, it is the P−V curves depicted in Figure 3, which are all much the same in the higher pressure region of interest, that should be tested experimentally rather than the precise values of B_0 and B_0' that can be used to generate these curves assuming the Birch−Murnaghan EOS.
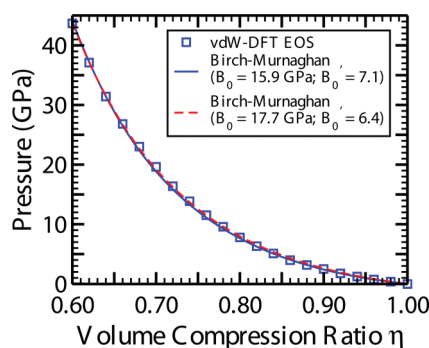
Figure 3. Computed vdW-DFT points (open squares) for the isothermal EOS for NEST-1 compared to values obtained from the Birch−Murnaghan EOS, assuming $B_0 = 15.9$ GPa and $B_0' = 7.1$ (solid line), and $B_0 = 17.7$ GP and $B_0' = 6.4$ (dashed line). The range in the volume compression ratio shown is $\eta = V/V_0 = 0.60$−1.00.

In summary, the hydrostatic EOS of the new energetic material NEST-1 was predicted by performing accurate calculations using vdW-corrected DFT. The results were successfully tested by comparing the equilibrium structural parameters with experiment. The high pressure data will be important for future mesoscale modeling of NEST-1, and should help stimulate experimental measurements of its EOS.

SUPPORTING INFORMATION AVAILABLE Figure and caption showing comparison of computed vdW-DFT data to corresponding experimental results for β-HMX, PETN-1, and α-RDX. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author:
*To whom correspondence should be addressed. E-mail: alanderv@shell.cas.usf.edu.

REFERENCES

(1) Chavez, D. E.; Hiskey, M. A.; Naud, D. L.; Parrish, D. Synthesis of an Energetic Nitrate Ester. *Angew. Chem., Int. Ed.* **2008**, *47*, 8307–8309.

(2) Neumann, M. A.; Perrin, M.-A. Energy Ranking of Molecular Crystals Using Density Functional Theory Calculations and an Empirical van der Waals Correction. *J. Phys. Chem. B* **2005**, *109*, 15531–15541.

(3) Kresse, G.; Furthmuller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54*, 11169–11186.

(4) Kresse, G.; Furthmuller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.

(5) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(6) Blochl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50*, 17953–17979.

(7) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59*, 1758–1775.

(8) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(9) Vinet, P.; Ferrante, J.; Smith, J. R.; Rose, J. H. A Universal Equation of State for Solids. *J. Phys. C* **1986**, *19*, L467–L473.

(10) Birch, F. Finite Elastic Strain of Cubic Crystals. *Phys. Rev.* **1947**, *71*, 809–824.

(11) Murnaghan, F. D. The Compressibility of Media under Extreme Pressures. *Proc. Natl. Acad. Sci. U.S.A.* **1944**, *30*, 244–247.

(12) Menikoff, R.; Sewell, T. D. Fitting Forms for Isothermal Data. *High Press. Res.* **2001**, *21*, 121–138.