

RESEARCH ARTICLE | MARCH 29 2012

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AIP Conf. Proc. 1426, 1191–1194 (2012)

<https://doi.org/10.1063/1.3686493>



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ACCURATE PREDICTION OF SECOND-ORDER ELASTIC CONSTANTS FROM FIRST PRINCIPLES: PETN AND TATB

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Abstract. We present preliminary results on the structural and mechanical properties of PETN and TATB as obtained by ab-initio calculations. While first principles approaches describe properties of materials occurring at 0 K, experimental results are mainly provided at ambient temperature. This difference leads to discrepancies in the desired agreement of calculated and measured properties. Also, the congenital limitations of DFT in dealing with long-range dispersion interactions, provide intrinsic limitations in this attempt. Our results are obtained through a full 3D approach that takes into account the van der Waals interaction in the form of London dispersion forces between the molecules assembled in the solid using the B3LYP-D* functional. Results are compared with available experiments and previous simulation data, showing very good agreement and validating the importance of including volume expansion effects in the description of molecular crystals at temperatures above absolute zero. To the authors' knowledge, the results presented for the elastic constants of TATB are the first ab-initio data for this energetic material.

Keywords: ab-initio, London forces, elastic constants, TATB.

PACS: 61.66.Hq, 62.20.-x, 61.50.Ah

INTRODUCTION

Energetic materials (EMs) such as explosives and propellants belong to the large family of so-called organic molecular crystals (OMCs), crystalline structures formed by stable molecules that stick together to form the solid mainly via hydrogen bonding and London long-range dispersion forces. Such *soft* structures can then be expected to be highly sensitive to thermodynamics conditions (volume, temperature and pressure) so that when an ab-initio approach is chosen, with the intent to accurately describe not only structures but also properties, one should take into account that calculations are performed at absolute zero (0 K)

while often, these systems are experimentally studied at room temperature (295 K).

Among others, the accurate description of mechanical properties of EMs is of high interest and plays an important role in the attempt to understand the physical-chemical nature of these materials. In particular, the capability of determining the full sets of second-order elastic constants (C_{ij}) allows one to completely address the mechanical nature of a crystalline system and can be used to understand and explain sensitivity and reactivity of materials under external mechanical stress. Experimentally and computationally, the complete and accurate determination of the full set of C_{ij} is still challenging; in fact, results obtained with different experimental techniques can vary

TABLE 1. PETN: Calculated and experimental lattice parameters (\AA), volumes (\AA^3) and densities (g cm^{-3}). T (in K) represents the temperature corresponding to the volume at which the structures have been optimized (calculations) and experimentally determined. ^a This work; ^b Ref [6]; ^c Ref [7]; ^d Ref [8].

	Calculations ^a				Experiments		
T	0	100	123	295	100 ^b	123 ^c	295 ^d
a	9.127	9.223	9.244	9.342	9.276(0)	9.303(0)	9.380
c	6.556	6.689	6.724	6.754	6.613(0)	6.640(0)	6.710
V	546.1	569.0	574.6	589.5	569.0	574.7	589.5
ρ	1.922	1.845	1.826	1.780	1.845	1.827	1.778

significantly because of limitations in sample purity and, similarly, different computational approaches can give different answers according to the level of theory considered.

In this work we report ab-initio results for structures and C_{ij} of tetragonal pentaerythritol tetranitrate ($\text{C}_5\text{H}_8\text{N}_4\text{O}_{12}$ – PETN) and triclinic triaminotrinitrobenzene ($\text{C}_6\text{H}_6\text{N}_6\text{O}_6$ – TATB). While PETN has been widely studied with different experimental and computational techniques, we could not find any available results for TATB, so that comparison is made with respect to the only available data obtained via a polarizable force field approach [1]. PETN was chosen as a benchmark to validate our approach (see next section); TATB to demonstrate the current capabilities of our ab-initio approach in accurately predicting structures and properties of low symmetry and weakly bonded crystalline systems.

COMPUTATIONAL METHODS

Calculations were performed via a periodic approach based on LCAO by using the B3LYP density functional corrected with an *a-posteriori* semi-empirical contribution [2] able to take into account long-range London dispersion forces in solids [3] as implemented in the CRYSTAL program [4]. We employed all-electrons 6-311G(d,p) basis sets for all the atoms; this choice shows to be a good compromise between accuracy of the results and request of computational resources.

As ab-initio calculations are performed at 0 K, in order to reproduce the experimental

thermodynamics conditions of the materials, we minimized the structures by imposing the experimental volume as corresponding to the reported temperature. Note that with this approach only the volume of the unit cell was kept constant, while both lattice parameters and atomic positions were allowed to relax. With this procedure, the volume corresponds to the experimental temperature at which the structure was resolved, and we can claim to *simulate* the temperature behavior of the system. Second-order elastic constants were determined through a recent implementation of the CRYSTAL program that computes the second derivative of the total energy with respect to the strain within an automatic scheme [5].

RESULTS AND DISCUSSION

Computed and experimental structural results for PETN are reported in Table 1 for lattice parameters, volumes and densities for geometries corresponding to 0 K, 100 K, 123 K, and 295 K. Cell parameters compared with respect to the same volume (i.e. temperature) show a general trend of our method in overestimating a of 0.5% on average, with a compensation in c showing an average underestimation equal to 1.0%. Nevertheless, the most important information comes from the value of the volume computed at 0 K compared with those obtained experimentally. In fact, the volumetric percent differences are 2.6, 3.6 and 7.9 for the volumes at 123, 100 and 0 K, respectively with respect to that at ambient temperature. With such discrepancy between the

standard ab-initio approach and in particular the value at ambient, one should expect physical properties to substantially differ.

TABLE 2. TATB: Calculated and experimental lattice parameters (\AA), volumes (\AA^3) and densities (g cm^{-3}). T (in K) represents the temperature corresponding to the volume at which the structures have been optimized (calculations) and experimentally determined. ^aThis work; ^bRef [9].

T	Calculations ^a		Experiments ^b
	0	295	295
a	8.976	9.061	9.01
b	9.075	9.172	9.028
c	6.381	6.546	6.812
α	108.9	107.4	108.6
β	91.9	90.9	91.8
γ	119.9	119.9	120.0
V	414.2	441.0	442.5
ρ	2.069	1.943	1.937

The same approach was adopted for TATB. At difference with PETN, we were able to find only one experimental structure at 295 K [9] so that in this case we can only report results at 0 K and at the volume corresponding to that obtained experimentally at ambient conditions (Table 2). Also in this case, the trend for the linear cell parameters is consistent with what one could expect when investigating a solid system at 0 K (more compact structure) with one at higher temperature (more expanded structure). Cell parameters a and b are underestimated on average by 1% while c compensates it with an overestimation of 4% allowing the volume of the unit cell to be kept constant to the experimental value (442.5 \AA^3). Once again, it is striking the big percent difference between the volume at 0 K and the experimental at 295 K (7%) so that one can easily expect properties computed at 0 K and ambient temperature to be different.

Given that the density (i.e. volume) varies substantially with respect to the temperature, one can expect properties depending upon the density

to change with a similar trend. This may be the case, for example, for C_{ij} and all the mechanical properties computed from them. Starting from the structures as optimized at different volumes corresponding to different temperatures, we determined the full set of elastic stiffness constants for PETN (reported in here) and TATB (for which we report only a subset). The tetragonal lattice of PETN and the triclinic of TATB will show six and twenty-one independent second-order elastic constants, respectively. Our C_{ij} results for PETN (0 K and 295 K) and partially for TATB (295 K) are reported in Table 3 and compared with Brillouin scattering [10] and polarizable force field simulations [1], respectively.

TABLE 3. TATB: Calculated and experimental lattice parameters (\AA), volumes (\AA^3) and densities (g cm^{-3}). T (in K) represents the temperature corresponding to the volume at which the structures have been optimized (calculations) and experimentally determined. ^aThis work; ^bRef [10]; ^cRef [11].

GPa / K	PETN			TATB	
	Calc ^a		Exp ^b	Calc ^a	Others ^c
	0	295	295	295	300
C_{11}	37.5	17.4	16.9	78.4	65.7
C_{33}	27.2	11.6	11.6	19.7	18.3
C_{44}	10.3	4.2	4.5	0.9	1.4
C_{66}	3.7	2.6	3.8	29.7	21.6
C_{12}	10.2	4.6	5.1	16.8	18.5
C_{13}	19.4	7.8	7.8	0.8	4.0

Our results for PETN corresponding to the volume at ambient temperature are in general very close to the experimental results; only in one case (C_{11}) we overestimate the Brillouin data. The worst agreement comes from the shear components C_{66} and C_{12} that refer to structures distorted in the a and b directions dominated by hydrogen bonding. As it appears for Table 1, our approach underestimates the a (b) cell parameter so that the trend reported for those two C_{ij} components may be due to our limits in describing the structural

behavior related to the hydrogen bonding directions.

From the full set of C_{ij} that we obtained for TATB, we report here only a small subset as the full discussion will be the subject of a future paper. As already mentioned, to the best of our knowledge experimental results for TATB are not available so that comparison will be done with respect to force field simulated results as reported in Ref [1]. In particular, we report two normal (C_{11} , C_{33}), two angular (C_{44} , C_{66}) and two dilational components (C_{12} , C_{13}). The TATB crystal is formed by molecules held together via hydrogen bond in the ab plane and London forces along the c crystal axes. This anisotropy is reflected by the much stiffer behavior of the crystal in the x and y directions (C_{11} , C_{22} – not reported) than in z (C_{33}); the same trend is reported from force field simulations. As the shear components are concerned, the two computational approaches show again similar trend in the results. Nevertheless, also in this case, values are quite different with our ab-initio data indicating a stiffer behavior for C_{66} . As the dilational components are concerned, both the approaches show that C_{12} gives the stiffest behavior when compared with C_{13} and C_{23} (not reported).

Despite the impossibility to compare our results with experiments, we think that data reported for the benchmark system PETN show how our approach can be taken as general, with the current available ab-initio approaches. From the full set of second-order elastic constants, it is easy to compute other mechanical properties such as bulk, shear, Young's moduli, Poisson's ratios and so forth. We would like to validate and extend this approach to other organic molecular crystals of interest for warfare, industrial and pharmaceutical applications.

ACKNOWLEDGEMENTS

Funding was provided by ONR (Grant N00014-01-1-0802). Calculations were performed on the ARSC computational resources.

REFERENCES

1. Bedrov, D., Borodin, O., Smith, G. D., Sewell, T. D., Dattelbaum, D. M., and Stevens, L. L., *J. Chem. Phys.* 131, 224703, 2009.
2. Grimme, S., *J. Comput. Chem.* 27, 1787, 2006.
3. Civalleri, B., Zicovich-Wilson, C. M., Valenzano, L., and Ugliengo, P., *Cryst. Eng. Comm.* 10, 405 2008.
4. Dovesi, R., Saunders, V. R., Roetti, R., Orlando, R., Zicovich-Wilson, C. M., Pascale, F., Civalleri, B., Doll, K., Harrison, N. M., Bush, I. J., D'Arco, P., and Llunell, M., *CRYSTAL09*, University of Torino, 2009.
5. Perger, W. F., Criswell, J., Civalleri, B., and Dovesi, R., *Comput. Phys. Com.* 180, 1753, 2009.
6. Zhurova, E. A., Stash, A. I., Tsirelson, V. G., Zhurov, V. V., Bartashevich, E. V., Potemkin, V. A., and Pinkerton, A. A., *J. Am. Chem. Soc.* 128, 14728, 2006.
7. Nieger, M., and Lehmann, J., *Cambridge Crystallographic Database*, 2002.
8. Cady, H. H., and Larson, A. C., *Acta Crystallogr. B* 31, 1864, 1975.
9. Cady, H. H., and Larson, A. C., *Acta Crystallogr.* 18, 485, 1965.
10. Stevens, L. L., Hooks, D. A., and Migliori, A., *J. Appl. Phys.* 108, 053512, 2010.