Structural and vibrational properties of nitrogen-rich energetic material guanidinium 2-methyl-5-nitraminotetrazolate

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ABSTRACT

We present density functional theory calculations on the crystal structure, equation of state, vibrational properties and electronic structure of nitrogen-rich solid energetic material guanidinium 2-methyl-5-nitraminotetrazolate (G-MNAT). The ground state structural properties calculated with dispersion corrected density functionals are in good agreement with experiment. The computed equilibrium crystal structure is further used to calculate the equation of state and zone-center vibrational frequencies of the material. The electronic band structure is calculated and found that the material is an indirect band gap semiconductor with a value of 3.04 eV.

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1. Introduction

Energetic materials have wide range of applications in both civilian and military sectors. For example, energetic materials are used in agriculture, mining, building demolition, pyrotechnics, coal blasting, tunneling, welding etc. Most importantly they are useful in fire fighting in war heads and as rocket boosters in aero space applications [1–4]. In general, energetic materials contain both fuel and oxidizer and reacts readily with the release of huge chemical energy stored within their molecular structures upon external stimulus such as heat, impact, shock, electric spark etc. The amount of energy released from an energetic material within a short time is considerably large when compared to the normal materials [5].

The detonation products of most of the energetic materials are water vapour, carbon monoxide CO, and carbon-di-oxide CO_2 [5,6]. These are well known green house gases that greatly affect the temperature of the earth. The best remedy for this problem is to have energetic materials that only give environmentally clean and eco-friendly detonation products. Nitrogen-rich compounds meet these demands quite well as they tend to show a high energy content and most importantly, their detonation products are pure nitrogen gas which is environment friendly [6]. Eremets et al., have synthesized polymeric nitrogen which is considered to be a green high energy density material [7]. Very recently, Fendt et al., synthesized tetrazole based nitrogen-rich energetic materials whose performance characteristics are found to be in good accord with well known high explosives [8]. In this family of compounds, guanidinium 2-methyl-5-nitraminotetrazolate ($C_3H_9N_9O_2$, G-MNAT) receives particular interest because of its similar energetic characteristics with that of 1,3,5-Trinitroperhydro-1,3,5-triazine ($C_3H_6N_6O_6$, RDX).

For any energetic material, the physical and chemical properties such as electronic band structure, bonding and vibrational properties are very important in order to understand the stability and thereby the sensitivity of the materials. These properties are directly related to the molecular packing, symmetry of the crystal structure and most importantly to the crystal density. Therefore it is quite essential to know about the crystal structure of the energetic materials and the structural modifications that occur upon the application of high pressures. Density Functional Theory (DFT) is a successful tool in simulating and predicting the physical and chemical properties of a wide spectrum of energetic materials [9–13]. However, most of the energetic materials have complicated crystal structures with weak inter molecular interactions and hence the investigation of different physical and chemical properties of energetic materials through DFT is really a challenging task [14]. In recent years, the advances in DFT methods have enabled us to describe effectively the materials with weak dispersive interactions [15,16]. There are few theoretical studies available based on dispersion corrected density functional methods to study the structural properties of various energetic materials [14]. To the best of our knowledge there are no theoretical reports available on solid G-MNAT. In this present work, we aim to study the crystal structure, equation of state and vibrational properties of solid G-MNAT. It is a well known fact that the electronic band gap plays a major role to understand the sensitivity of energetic materials [17]. Hence, we also calculate the energy band structure and the variation of band gap with pressure. The remainder of the Letter is organized as follows: A brief description of our computational details is presented in Section 2. The results and discussion are presented in Section 3 followed by summary of our conclusions in Section 4.

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2. Computational details

The calculations are performed using plane wave pseudopotential method based on density functional theory [18]. The interactions between the ions and electrons are described by using Vanderbilt ultrasoft pseudopotentials [19]. For all the calculations we have included the $1s^1$ electrons for hydrogen, $2s^2$, $2p^2$ electrons for carbon, $2s^2$, $2p^3$ electrons of nitrogen and the $2s^2$, $2p^4$ states of oxygen. Both local density approximation (LDA) of Ceperley and Alder [20] parameterized by Perdew and Zunger (CA–PZ) [21] and also the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) [22] parameterization are used for the exchange–correlation potentials. The calculations are performed using an energy cut-off of 640 eV for the plane wave basis set. Integrations in the Brillouin zone are performed according with a $5 \times 3 \times 2$ Monkhorst–Pack grid scheme [23] k-point mesh. The changes in the total energies with the number of k-points and the cut-off energy are tested to ensure the convergence within one meV per atom.

To treat van der Waals (vdW) interactions efficiently, we have used the vdW correction to the exchange–correlation functional of standard density functional theory at semi-empirical level. According to semi-empirical dispersion correction approach, the total energy of the system can be expressed as

$$E_{total} = E_{DFT} + E_{Disp} \tag{1}$$

where

$$E_{Disp} = s_i \sum_{i=1}^{N} \sum_{j>i}^{N} f(S_R R_{ij}^0, R_{ij}) C_{6,ij} R_{ij}^{-6} \tag{2}$$

here $C_{6,\ ij}$ is called dispersion coefficient between any atom pair i and j which solely depends upon the material and R_{ij} is the distance between the atoms i and j. In the present Letter we have used the recently developed dispersion schemes by Grimme [15], Tkatchenko–Scheffler [16] within GGA. These semi-empirical approaches provide the best compromise between the cost of first principles evaluation of the dispersion terms and the need to improve nonbonding interactions in the standard DFT description.

3. Results and discussion

3.1. Structural properties

At ambient pressure, solid G-MNAT exists in monoclinic structure with space group $P2_1$ and contain two molecules per unit cell ($z = 2$) [8]. The experimental crystal structure is taken as starting input for the calculations and then we apply standard density functionals LDA (CA–PZ), GGA (PBE) and also the dispersion corrected density functionals PBE + TS and PBE + G06 to get the theoretical equilibrium structure. The calculated lattice parameters are presented in Table 1 together with the experimental values [8]. The computed crystal volume is underestimated by -8.3% using CA–PZ functional and overestimated by 7.1% with PBE computation.

This large discrepancy is due to the fact that the present studied compound is a molecular solid with weak dispersion forces for which the usual LDA and GGA functionals are inadequate to treat these forces. On the other hand, the computation carried out by dispersion corrected density functionals describe well the crystal structure and the computed volume is in good agreement with experiment. The equilibrium crystal volume is overestimated by 1.7% using PBE + TS functional and underestimated by -0.6% with PBE + G06 functional. Clearly, the dispersion corrected density functionals are efficient to describe the crystal structure of G-MNAT. This is supported by the earlier theoretical studies on energetic solids where the authors found that the intermolecular interactions were well described by the dispersion corrected density functionals [14]. In particular, the PBE + G06 functional describes the solid G-MNAT system with less error compared to PBE + TS functional. Thus, for all rest of the calculations we use PBE + G06 functional.

The optimized crystal structure of G-MNAT and its molecular structure using PBE + G06 functional are shown in Figure 1(a) and (b) respectively. The calculated bond lengths between N1—N2, N2—N3, and N3—N4 are found to be 1.35 Å, 1.34 Å and 1.33 Å respectively. These are in good agreement with experimental bond length values that varies between 1.30 and 1.33 Å [8]. The torsion angle C1—N2—N3—N4 is calculated to be $-0.246°$ which is in good comparison with experimental value of $-0.3°$ [8]. The bond lengths between the C1—N1, C1—N4 and C2—N2 are calculated to be 1.36 Å, 1.37 Å, 1.45 Å. It should be note that the calculated values of bond lengths between N atoms and C, N atoms are comparable to that of the bond lengths of N—N (1.45 Å), N=N (1.25 Å), C—N (1.47 Å) and C=N (1.22 Å) respectively.

(a)

(b)

Figure 1. Crystal structure of G-MNAT (a). In figure grey ball, white ball, blue ball and red ball indicates, carbon, hydrogen, nitrogen and oxygen atoms respectively. (b) Molecular structure of G-MNAT. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
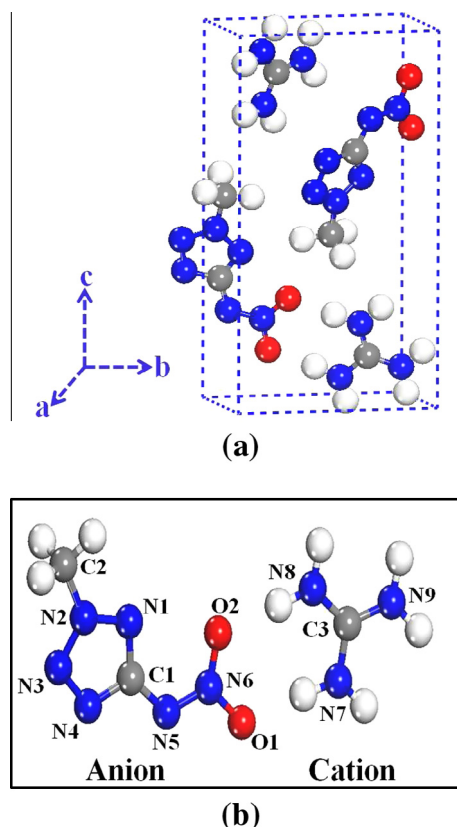
Table 1
Ground state structural properties of crystalline guanidinium 2-methyl-5-nitraminotetrazolate (G-MNAT) calculated using various exchange–correlation functionals. Experimental data have been taken from Fendt et al. [8].

XC functional	a (Å)	b (Å)	c (Å)	β°	ρ (gm/cc)	V (Å³)
CA–PZ	3.5167	7.8685	13.7515	94.44	1.778	379.38
PBE	4.7258	7.6277	15.1658	105.96	1.284	525.61
PBE + TS	3.7123	8.0569	14.1369	95.43	1.603	420.91
PBE + G06	3.6111	8.0296	14.2334	95.35	1.642	410.91
Expt	3.6562	8.1552	13.9458	95.91	1.631	413.61
	B_0				B_0'	
PBE + G06	15.3				4.66	