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First-principles study of the high-pressure behavior of solid 1,7-diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane

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ABSTRACT

The structural, electronic, and absorption properties of crystalline 1,7-diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane (APX) in the pressure range of 0–20 GPa have been studied by using density functional theory. A comprehensive analysis of the variation trends of the lattice constants, bond lengths, bond angles, and intra-molecular H-bonds under compression indicates that there are four structural transformations in APX at 2, 4, 10, and 19 GPa, respectively. Structural transformations occurred at 2 and 10 GPa weaken the H-bonding. The impact sensitivity for APX becomes more and more sensitive with the increment of pressure. An analysis of density of states suggests that the band splitting and dispersion increase due to the enhanced intermolecular interactions at high pressures. APX has relatively high optical activity at high pressure. The structural transformation at 4 GPa makes the absorption coefficient of the C–H stretching increase significantly, but the transformations at 2 and 19 GPa decrease that slightly.

1. Introduction

The performance of high explosives depends on several main factors including crystal density and morphology, thermal stability, detonation velocity and pressure, and chemical reactivity, but these factors are ultimately dominated by their solid-state structure. In order to understand the properties of high explosives under different conditions, it is necessary to obtain the structure information over a range of temperature and pressure, especially under high pressure or high temperature. This is because a shock wave with high velocity through an explosive during detonation can result in a pressure of 50 GPa and a temperature of 5500 K within the explosive [1]. Under such extreme conditions, the explosive is expected to experience phase transitions or decomposition reactions [2–5]. In addition, the information of explosive under extreme conditions can also provide useful guidance for its safe use and disposal.

Recently, Altenburg et al. [6] synthesized a new high explosive 1,7-diamino-1,7-dinitrimino-2,4,6-trinitro-2,4,6-triazaheptane (APX, $C_4H_8N_{12}O_{10}$, as shown in Fig. 1) with a crystal density of 1.911 g/cm^3. APX decomposes at 174 °C and its experimentally impact, friction, and electrostatic discharge sensitivities are 3 J, 80 N, and 0.1 J, respectively. It is a derivative of 1,2-dinitroguanidine and its predicted detonation velocity and detonation pressure are 9540 m/s and 39.5 GPa, respectively, which are even better than those of commonly used explosive 1,3,5,7-tetranitro-1,3,5,7-tetraazoctane (HMX). Liu et al. [7] reported that APX possesses good thermal stability. Since APX has high sensitivity, it can be used as an initial explosive. Although its high sensitivity would restrict its synthesis and application, its sensitivity can be reduced by coatings or mixing with binder systems like PVAA (polyvinyl alcohol acetate). Thus, it can be used as the energetic filler in high explosive formulations for its high detonation performances. [6] The biggest difference between APX and common used explosives like HMX is its special long-chain structure. This can make it has obviously different properties to the explosives with cyclic structure. Therefore, further studies about APX are not only important for its safety application, but also provide useful information for developing new explosives with chain structure. Since no work on its behavior under high pressure has been done, there is a clear need to gain an understanding of that at the ab initio level.

The investigation of microscopic properties of energetic materials, which possess a complex chemical behavior, remains to be a challenging task. It is very difficult to carry out high-pressure experiments on high explosives. Theoretical calculations are an effective way to model the physical and chemical properties of complex solids at the atomic level as a complement to experimental work. Recently, density functional theory (DFT) method with pseudopotentials and a plane-wave basis set has been well-established and has been applied successfully to study the structures and properties of energetic solids under hydrostatic compression [8–12].

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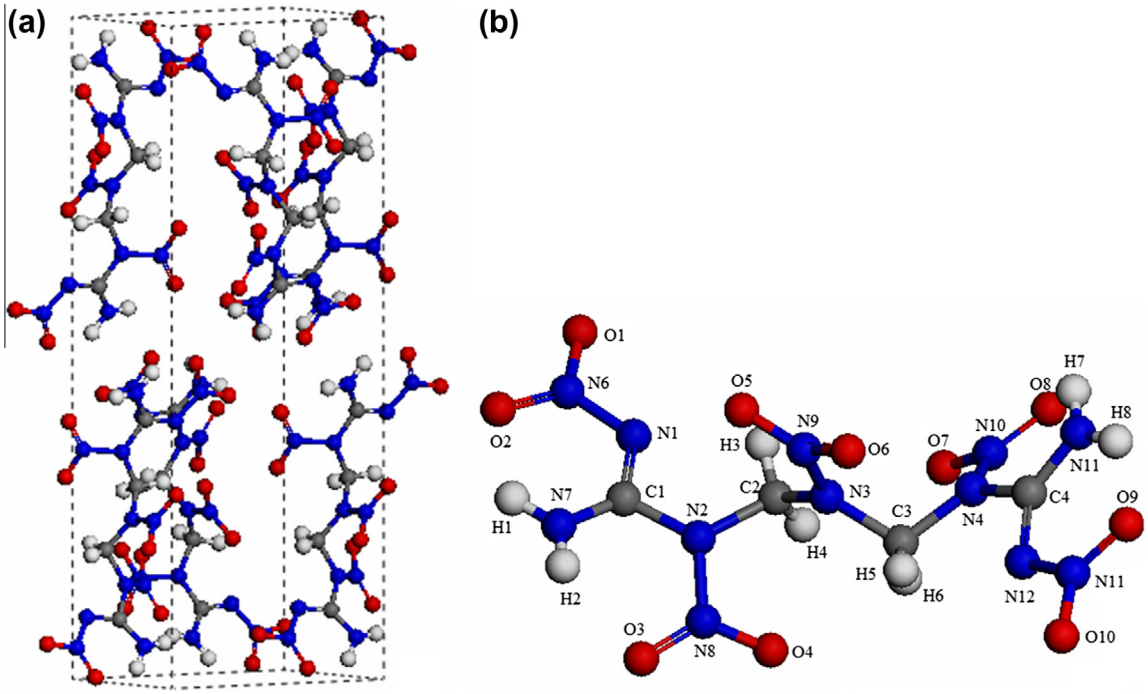

Fig. 1. Crystal structure (4 molecules) and molecular structure ($C_4H_8N_{12}O_{10}$) of APX. The white, red, blue, and gray spheres stand for H, O, N, and C atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In this study, we performed periodic DFT calculations to study the structural, electronic, and absorption properties of APX crystal under hydrostatic pressure of 0–20 GPa. To investigate the crystal structure at different pressures, the atomic positions and the unit-cell parameters were allowed to relax to the minimum energy. Then we examined their variations in the structural and properties under different pressures.

2. Computational method

The calculations performed in this study were done within the framework of DFT based on CASTEP code [13], using Vanderbilt-type ultrasoft pseudopotentials [14] and a plane-wave expansion of the wave functions. The self-consistent ground state of the system was determined by using a band-by-band conjugate gradient technique to minimize the total energy of the system with respect to the plane wave coefficients. The electronic wave functions were obtained by using a density-mixing minimization method [15] for the self-consistent field calculation and the structures were relaxed by using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) [16] method. Geometry optimization is based on reducing the magnitude of calculated forces and stresses until they become smaller than convergence tolerances. Therefore, it is possible to specify an external stress tensor to model the behavior of the system under tension, compression, shear, etc. In these cases the internal stress tensor is iterated until it becomes equal to the applied external stress. The LDA functional proposed by Ceperley and Alder [17] and parameterized by Perdew and Zunder [18], named CA-PZ, was employed. The cutoff energy of plane waves was set to 340 eV. Brillouin zones sampling was performed by using the Monkhost–Pack scheme with a *k*-point grid of $2 \times 2 \times 1$. The values of the kinetic energy cutoff and the *k*-point grid were determined to ensure the convergence of total energies.

In order to compare with experiments, we used the crystal structure of APX at ambient pressure and temperature as input structure. APX crystallizes in an orthorhombic lattice with *Pbcn* space group and contains four $C_4H_8N_{12}O_{10}$ molecules per unit cell [6]. Fig. 1 displays crystal and molecular structures of APX. The experimental crystal structure of APX [6] was first relaxed to allow the ionic configurations, cell shape, and volume to change at ambient pressure. Then from this relaxed structure, we applied hydrostatic compression of 1–20 GPa to relax the crystal structure without any symmetry constraints. All the calculations are based on the same crystal structure of APX. In the geometry relaxation, the total energy of the system was converged less than 2.0×10^{-5} eV, the residual force less than 0.05 eV/Å, the displacement of atoms less than 0.002 Å, and the residual bulk stress less than 0.1 GPa. Previous studies employing the same approach to simulate the hydrostatic compression of energetic crystals [19–20] indicate that the calculated results were in agreement with the experiments.

3. Results and discussion

Our previous studies on energetic crystals [10–12,19] have shown that the LDA functional can produce more reliable geometrical structures than the GGA (generalized gradient approximation). As a benchmark, the LDA/CA-PZ and GGA/PW91 (Perdew-Wang 91) [21] were selected to fully relax APX crystal at ambient pressure without any constraints. Table 1 lists the experiment and relaxed cell parameters of APX crystal. It is found that the errors in the LDA results are much smaller than those in the GGA ones in comparison with the experimental values. Table 2 presents the LDA/CA-PZ-calculated bond lengths and bond angles of APX along with corresponding experimental data. It is seen that the bond lengths and bond angles compare well with experimental values, indicating that the LDA/CA-PZ method is reasonably satisfactory for studying APX crystal. Thus, the LDA (CA-PZ) method was employed in this study.

3.1. Crystal structure

Both experimental and computational studies [8,10,22,23] indicated that the external pressure can induce the changes of