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DFT study on the structures and properties of 3-nitro-1,2,4-triazol-5-one crystals at high pressure

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Abstract

The geometries, lattice parameters, electronic structures, XRD spectra and optical properties of the 3-nitro-1,2,4-triazol-5-one (NTO) crystals at high pressure (2, 4, 6, 8 and 10 GPa) have been studied using density functional theory within the generalized gradient approximation implemented using ultrasoft pseudo-potentials. The computational results show that with increasing pressure, the NTO lattice parameters and hydrogen bonds lengths rapidly decrease and the geometries change very little. The total energy increases by approximately 27.543 eV from 0 to 10 GPa. NTO becomes increasingly conductive or metallic with increasing pressure, while the XRD peaks are shifted to greater angles and the absorption coefficient $\alpha(\omega)$ increases.
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Keywords: 3-Nitro-1,2,4-triazol-5-one (NTO); Density functional theory; XRD spectra; Optical properties

1. Introduction

3-Nitro-1,2,4-triazol-5-one (NTO) is a well-known insensitive high explosive (IHE). Since this compound was first prepared, it has been investigated in a number of experimental and theoretical studies [1–27]. It was characterized as a potential high energy density material (HEDM) that is powerful yet resistant to accidental and sympathetic initiation. Its crystalline structure has been theoretically and experimentally investigated. Sorescu and Thompson developed an intermolecular potential to describe the structure of NTO crystal using rigid molecules [15]. Xiao used the periodic DFT-B3LYP technique to investigate the intermolecular interaction in the bulk state of NTO [16]. However, to date there has been no report on a systemic study of NTO crystalline structures under high isostatic pressure. Crystalline structures determine crystalline properties. There is great interest in NTO crystalline structures under high detonation pressures or other extreme conditions, but it is very difficult or impossible to study these experimentally. In this study we used ab initio periodic calculation methods based on density functional theory to study the equilibrium geometries, lattice parameters, electronic structures, XRD spectra and optical properties of NTO crystal at high isostatic pressure. These information will be helpful for the study and molecular design of energetic compounds.

2. Computational methods

The calculations in this study were performed within the framework of DFT [28] using Vanderbilt-type ultrasoft pseudo-potentials [29] and a plane-wave expansion of the wave functions. The self-consistent ground state of the system was determined using a band-by-band conjugate gradient technique to minimize the total energy of the system with respect to the plane-wave coefficients at different external pressures of 0, 2, 4, 6, 8 and 10 GPa. The electronic wave functions were obtained using a density-mixing scheme [30] and the structures were relaxed using the Broyden–Fletcher–Goldfarb–Shannon

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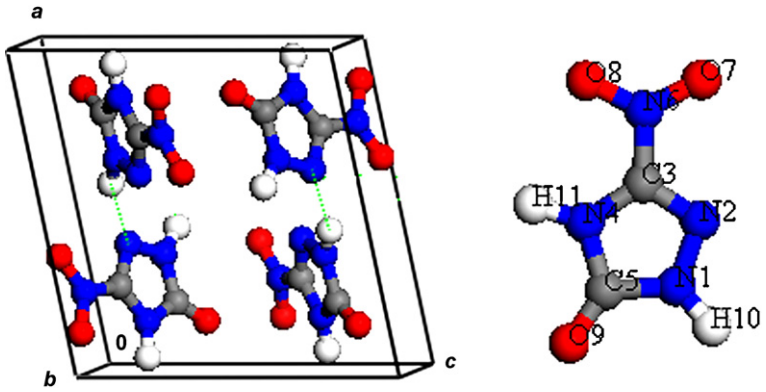

Fig. 1. Packing and atomic numbering of β-NTO in the unit cell. Carbon, nitrogen, oxygen, and hydrogen atoms are represented in gray, blue, red, and white, respectively.

(BFGS) method [31]. The generalized gradient approximation (GGA) with PW91 was employed. We adopted the experimental structure (Fig. 1) from Ref. [5] as the initial structure. All calculations were carried out by using CASTEP code [32]. The cutoff energy for plane waves was set to 300.0 eV. Brillouin zone sampling was performed using the Monkhost–Pack scheme with a *k*-point grid of 2 × 4 × 2. The values of the kinetic energy cutoff and the *k*-point grid were determined to ensure the convergence of total energies to within 0.01%. In the geometry relaxation, the total energy of the system converged to less than 1.0×10^{-6} eV, the residual force to less than 0.02 eV/Å, the displacement of atoms to less than 0.001 Å, and the residual bulk stress to less than 0.1 GPa.

3. Results and discussion

3.1. Crystal structure

We concentrated on pressures between 0 and 10 GPa and assumed that there is no phase transition in this region. Full relaxation of the structure was performed to allow the NTO molecular configurations, cell shape and volume to change. The results for all the geometric parameters, including the lattice vectors, are shown in Table 1.

Table 1 shows that although *a*, *b* and *c* decrease with increasing external pressure, *c* decreases much more rapidly than *a* and *b* and the *c*/*a* ratio decreases from 0.990 at 0 GPa to 0.977 at 4 GPa and to 0.969 at 10 GPa, which indicates anisotropic changes in the crystal under high pressures. Another decrease in the NTO crystal size is also revealed by the magnitude of the shortening of hydrogen bonds. Table 1 shows that the O–H hydrogen bond length changes from 1.702 to 1.638 to 1.565 Å as the pressure changes from 0 to 4 to 10 GPa, whereas the N–H hydrogen bond distance changes from 2.090 to 2.004 to 1.879, respectively.

Compared with the changes in lattice parameters and hydrogen bond lengths, the bond lengths within an NTO molecule vary much less (more than 100-fold less) with changes in the external pressure. Some bond lengths, such as C–O and N–H, increase, whereas others, such as C–N, N–N and

Table 1
Cell and geometric parameters for NTO crystals at different external pressures

Parameter	0 (GPa)	2 (GPa)	4 (GPa)	6 (GPa)	8 (GPa)	10 (GPa)	Exp. [5]
a (Å)	9.435	9.312	9.255	9.192	9.134	9.089	9.325
b (Å)	5.591	5.484	5.439	5.398	5.353	5.307	5.450
c (Å)	9.336	9.119	9.040	8.970	8.891	8.806	9.040
b/*a*	0.593	0.589	0.588	0.587	0.586	0.584	0.584
c/*a*	0.990	0.979	0.977	0.976	0.973	0.969	0.969
β (°)	101.4	101.4	101.5	101.6	101.6	101.6	101.5
N1–N2 (Å)	1.353	1.353	1.352	1.352	1.351	1.351	1.366
N1–C5 (Å)	1.381	1.379	1.378	1.375	1.372	1.372	1.374
N1–H10 (Å)	1.029	1.033	1.035	1.036	1.039	1.039	1.009
N2–C3 (Å)	1.306	1.306	1.306	1.306	1.305	1.305	1.299
C3–N4 (Å)	1.350	1.348	1.347	1.345	1.341	1.341	1.356
C3–N6 (Å)	1.416	1.414	1.413	1.411	1.408	1.408	1.443
N4–C5 (Å)	1.376	1.373	1.371	1.369	1.366	1.366	1.375
N4–H11 (Å)	1.051	1.052	1.054	1.057	1.061	1.061	1.009
C5–O9 (Å)	1.230	1.232	1.232	1.232	1.234	1.234	1.234
N6–O7 (Å)	1.252	1.251	1.251	1.251	1.250	1.250	1.227
N6–O8 (Å)	1.248	1.248	1.248	1.247	1.247	1.247	1.225
N···H (Å)	2.090	2.045	2.004	1.964	1.918	1.879	2.054
O···H (Å)	1.702	1.667	1.638	1.607	1.582	1.565	1.723

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