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Density functional theory study of structural, vibrational, and thermodynamic properties of crystalline 2,4-dinitrophenol, 2,4-dinitroresorcinol, and 4,6-dinitroresorcinol

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ABSTRACT

The electronic structure, vibrational properties, and thermodynamic properties of crystalline 2,4-dinitrophenol, 2,4-dinitroresorcinol, and 4,6-dinitroresorcinol have been comparatively studied using density functional theory in the local density approximation. An analysis of electronic structure shows that there is good electronic delocalization in the three solids. The motions of the NO_2 groups in the three solids are diffusely distributed. The calculated thermodynamic properties show that the decomposition reactions of the three solids are thermodynamically favorable under high temperature; moreover, 2,4-dinitrophenol has higher possibility to decompose than 2,4- and 4,6-dinitroresorcinol.

1. Introduction

Nitro phenols are a class of nitro compounds generally known as explosives and often classified as secondary explosives [1,2]. Many experimental and theoretical studies [3–14] are performed to investigate the structures and vibrational properties of nitro phenols. Among these compounds, 2,4-dinitrophenol is commercially important and primary used as a chemical intermediate for the production of azo dyes, wood preservatives, and pesticides. Another polyhydric phenol of important industrial use is dinitroresorcinol. Two isomers exist, 2,4- and 4,6-dinitroresorcinol. For crystalline 2,4-dinitrophenol, 2,4-dinitroresorcinol, and 4,6-dinitroresorcinol, there is a variation in the stability to impact and shock.

A desire to probe more fundamental questions relating to the basic properties of the three solids as energetic materials is generating significant interest in their basic solid-state properties. The electronic structure is intimately related to their fundamental physical and chemical properties; moreover, an understanding of electronic structure and properties is necessary for discussion of electronic processes as they relate to decomposition and initiation. On the other hand, although the detailed decomposition mechanism by which the three solids release energy under mechanical shock is still not well understood, it has been suggested that their decomposition may result from transferring thermal and mechanical energy into the internal degrees of freedom of tightly bonded groups of atoms in solids [15–17]. Therefore the knowledge of their electronic and properties appears to be very important in understanding their explosive properties. The investigation of the microscopic properties of energetic materials, which possess a complex chemical behavior, remains to be a challenging task. 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.

In this study we performed periodic density functional theory (DFT) calculations to study the electronic structure, vibrational properties, and thermodynamic properties of crystalline 2,4-dinitrophenol, 2,4-dinitroresorcinol, and 4,6-dinitroresorcinol. Our main purpose here is to examine the differences in the electronic structure and properties among them.

The remainder of this paper is organized as follows. A brief description of our computational method is given in Section 2. The results and discussion are presented in Section 3, followed by a summary of our conclusions in Section 4.

2. Computational method

The calculations performed in this study were done using the CASTEP code [18] based on DFT with Vanderbilt-type ultrasoft pseudopotentials [19] 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

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to minimize the total energy of the system with respect to the plane-wave coefficients. The electronic wave functions were obtained by a density-mixing scheme [20] and the structures were relaxed by using the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) method [21]. The local density approximation (LDA) functional proposed by Ceperley and Alder [22] and parameterized by Perdew and Zunder [23] named CA-PZ, was employed. The cutoff energy of plane waves was set to 500.0 eV. Brillouin zone sampling was performed by using the Monkhost–Pack scheme with a k-point grid of $3 \times 1 \times 4$, $4 \times 3 \times 1$, and $2 \times 4 \times 2$ for 2,4-dinitrophenol, 2,4-dinitroresorcinol, and 4,6-dinitroresorcinol, respectively. The values of the kinetic energy cutoff and the k-point grid were determined to ensure the convergence of total energies.

2,4-Dinitrophenol crystallizes in an orthorhombic $P2_12_12_1$ space group and contains four molecules per unit cell [24]. 2,4-Dinitroresorcinol crystallizes in a orthorhombic space group, $P2_12_12_1$, with four molecules per unit cell [25]. 4,6-Dinitroresorcinol crystallizes in a monoclinic space group, $P2_1/c$, with four molecules per unit cell [26]. There is strong intramolecular hydrogen bonding involving hydrogen atoms of hydroxyls with the oxygen atoms of nitro groups in the three solids. Fig. 1 displays the unit cells of the three crystals, and conformations and atomic numberings of molecules in the solid phases are shown in Fig. 2.

Starting from the above-mentioned experimental structures, the geometry relaxation was performed to allow the ionic configurations, cell shape, and volume to change. 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. For all the relaxed structures, the Mulliken charges and bond populations were investigated using a projection of the plane-wave states onto a linear combination of atomic orbitals (LCAO) basis set [27,28], which is widely used to perform charge transfers and populations analysis. The phonon frequencies at the gamma point have been calculated from the response to small atomic displacements [29].

3. Results and discussion

3.1. Bulk properties

In our previous study [30] we applied three different functionals: LDA (CA-PZ) and generalized gradient approximation (GGA) (Perdew–Burke–Ernzerhof (PBE) [31] and Perdew–Wang 91 (PW91) [32]), to molecular crystal octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) as a test and found that the LDA may be expected to produce more reliable predictions of the structures. Since 2,4-dinitrophenol, 2,4-dinitroresorcinol, and 4,6-dinitroresorcinol are molecular crystals, LDA was used in all calculations here. The calculated cell parameters, bond lengths, and bond angles of 2,4-dinitrophenol, 2,4-dinitroresorcinol, and 4,6-dinitroresorcinol are given in Table 1 together with their experimental results. The calculated results reproduce the measured cell parameters of the three solids. The differences between the calculated and experimental values are typical for the LDA approximation to DFT. We also note that the calculated bond lengths and bond angles are very close to the corresponding experimental data except the N—O bond lengths. These discrepancies between the calculated and experimental N—O bond lengths may be due to intermolecular and intramolecular hydrogen bonding interactions present in the crystal lattice, which are not well described by DFT. These comparisons confirm that our computational parameters are reasonably satisfactory.

3.2. Electronic structure

The calculated total density of states (DOS) and partial DOS (PDOS) for 2,4-dinitrophenol, 2,4-dinitroresorcinol, and 4,6-dinitroresorcinol are displayed in Figs. 3–5, respectively. Clearly, the structures are very similar except some subtle differences. The DOS of the three solids are finite at the Fermi energy level. This is because the DOS contain some form of broadening effect. In the upper valence band, the three solids have a sharp peak near the Fermi level. The top of the DOS valence band shows four main peaks for 2,4-dinitrophenol, three main peaks for 2,4-dinitroresorcinol, and three main peaks for 4,6-dinitroresorcinol. These peaks are predominately from the p states. After that, several main peaks in the upper valence band are superimposed by the s and p states. The conduction band is dominated by the p states. This indicates that the p states for the three solids play a very important role in their chemical reaction. Note that several DOS peaks in the upper valence band merge together, showing that there is good electronic delocalization in the systems. This is because the bonding in the ring is formally aromatic.

The atom-resolved DOS and PDOS of 2,4-dinitrophenol, 2,4-dinitroresorcinol, and 4,6-dinitroresorcinol are also shown in Figs.

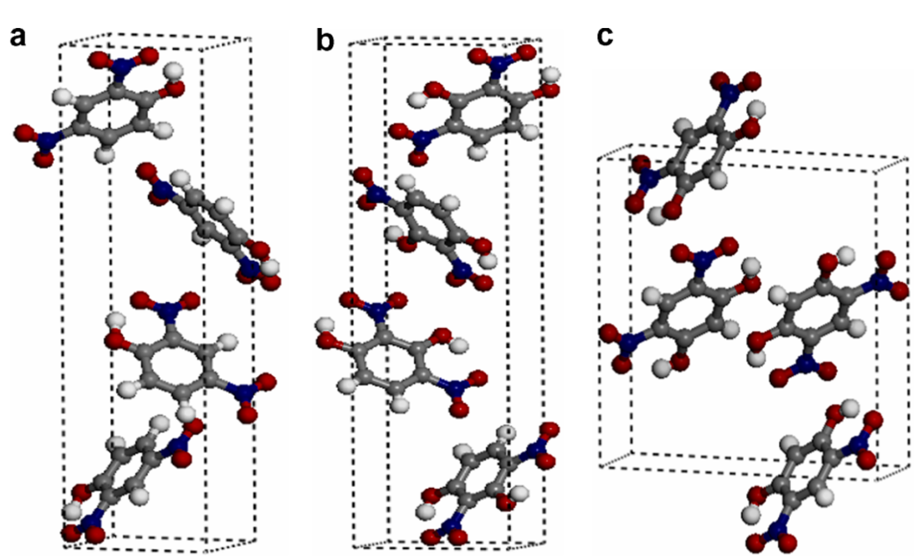

Fig. 1. Unit cells for (a) 2,4-dinitrophenol, (b) 2,4-dinitroresorcinol, and (c) 4,6-dinitroresorcinol crystals.