Structural and electronic properties of 5,5′-Hydrazinebistetrazole under high pressure: A DFT study

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Abstract. We have investigated the effect of pressure on the structural and electronic properties of 5,5′-Hydrazinebistetrazole (HBTA) up to 25 GPa using first principles calculations. The recently developed van der Waals density functional approach (optB88-vdW) have been employed for the accurate description of intermolecular interactions. The obtained theoretical lattice constants and volume are consistent with the experimental data under the studied pressure range. The electronic structure calculations using Tran-Blaha modified Becke Johnson (TB-mBJ) potential show that HBTA is an indirect band gap insulator (4.31 eV) along Γ-Z direction and the gap is found to decrease gradually as a function of pressure. The Hirshfeld surfaces analysis and the corresponding 2D fingerprint plots show reduction in the N...H/H...N contribution, which supports the experimentally reported weakening of hydrogen bonding under pressure.

1. Introduction
The development of green energetic materials (EM) is a continuous process to meet the growing requirements of defense applications. However, the performance of an explosive mainly depend on its density, oxygen balance and heat of formation, which are partially governed by its molecular structure[1]. In one way we can improve the performance of EM through nitrogen rich heterocyclic compounds that can increase the heat of formation and thus performance. On the other hand, the best approach to counteract the correlation of high performance with high sensitivity to friction, impact and shock is by choosing the systems with strong hydrogen bonding networks which can provide compact packing within the crystal leading to better density and stability of the system[2]. More interestingly, the presence of C-N and N-N bonds in high nitrogen content EM not only provide high positive heat of formation but also forms more number of hydrogen bonds, which allows the material to obtain high densities, good thermal stabilities and low sensitivities. Especially, nitrogen rich azoles are considered to be promising candidates for the construction of future high energetic materials[3, 4].

The presence of intermolecular N-H...N hydrogen bonding interactions between two tetrazole rings increase the density of a material there by providing high performance with low sensitives[5]. In addition, The effect of pressure on the density of a material plays a crucial role in determining the performance of an explosive. At a particular pressure range, the energetic
Figure 1. (a) The crystal structure of HBTA, (b) molecular geometry with atomic numbering, (c) Hydrogen bond architecture in HBTA. The dashed lines represents the hydrogen bond interactions.

material has an higher density, leading to larger detonation pressure and velocity[6]. Therefore, the high pressure studies, especially on hydrogen bonded EM are important to understand the structural stability of materials for their better performance and applications. In the present work, we have reported the structural and electronic properties of 5,5′-Hydrazinebistetrazole (HBTA) as a function of pressure up to 25 GPa using density functional theory (DFT).

2. Methodology
We performed ab initio calculations with the periodic plane-wave basis set as implemented in VASP code[7]. The projector augmented wave (PAW) potential have been used to describe the core and valence electrons interactions, with a cutoff energy of 600 eV. The functional developed by Perdew, Burke, and Ernzerhof (PBE)[8] based on the generalized gradient approximation is used to describe the exchange-correlation energy. The system is relaxed until the atomic forces on every atom were < 0.01 eV/Å. For sampling the reciprocal space, we used 5×5×3 Monkhorst-Pack k-point grid [9]. In order to include van der Waals interactions accurately within the system, optB88-vdW-DF functional[10] is used. To overcome the long standing problem of band gap underestimation using standard DFT functional, we implemented the modified version of Tran and Becke exchange potential[11], which can provide more accurate energy bands. Hirshfeld surfaces and the corresponding 2D-fingerprint plots were analysed using the software CrystalExplorer 3.1[12].

3. Structural properties
HBTA crystalizes in the monoclinic C2/c symmetry with four formula units. The crystal structure and three dimensional hydrogen bonding interaction of HBTA along with atomic labels for all the inequivalent atoms present in the molecule are shown in the Figure 1. The two tetrazole rings are linked by NH-NH group. Each molecule of HBTA consists of eight hydrogen bonds with a distance of nearly 2.93Å. The strong hydrogen bonding interactions present in the crystal pulls the structure to be closely packed to obtain higher crystal density of 1.84 g/cm³[13], which is greater than that of well known explosive 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX, 1.82 g/cm³)[14]. The denotation velocity of HBTA (8523 m/s)[15] is smaller than the value
of RDX with an impact sensitivity $>30$ J and friction sensitivity $>360$ N[16]. In spite of its high nitrogen content (83.3%), the presence of extensive hydrogen bonding networks makes the material insensitive and thermally stable[13]. Moreover, nitrogen gas is the major decomposition product in HBTA as shown by Mass spectrometry measurements[16].

![Graphs showing lattice parameters, volume, and density of HBTA as a function of pressure. Experimental values are shown in dotted lines for comparison[18].](image)

Figure 2. Calculated (a) lattice parameters (b) volume (c) density of HBTA as a function of pressure. Experimental values are shown in dotted lines for comparison[18].

The experimental structure of HBTA is optimized by fully relaxing the lattice parameters and atomic coordinates using optB88-vdW functional. The obtained results agrees well with the experimental values and we proceed with the optB88-vdW method for the high pressure calculations. The calculated lattice parameters, volume and density of HBTA as a function of pressure along with experimental results are shown in the Figure 2. The theoretical lattice constants are consistent with the experimental data under the studied pressure range. The effect of hydrostatic pressure on the crystal show the anisotropic compressibility in the lattice constants. We could not observe any discontinuity in the lattice parameters as a function of pressure up to 25 GPa. As shown in Figure 2b, the volume of HBTA found to decreases monotonically with pressure, which results in rapid increase in the crystal density ($\rho = 1.89$ g/cm$^3$ at 0GPa, $\rho = 2.66$ g/cm$^3$ at 25 GPa, see Figure 2c). We also calculated the bulk modulus ($B_0$) and its pressure derivatives ($B'_0$) by fitting the pressure-volume data to the third order Birch Murnaghan equation of state[17]. The obtained $B_0$ and $B'_0$ values are found to be 27.78 GPa and 5.82, respectively, which are slightly higher than the experimental values ($B_0 = 21.8$ GPa, $B'_0 = 3.8$)[18].

4. Electronic properties
The band gap is an essential property to characterize the electronic structure of energetic materials which is used to correlate the photo sensitivity. However, the standard DFT functionals are unable to predict the electronic band gap values accurately. In order to overcome this problem, we employed the recently developed Tran-Blaha modified Becke Johnson (TB-mBJ)[11] potential for electronic structure calculations of HBTA as a function of pressure up to 25 GPa. Figure 3 presents the calculated total and partial density of states (DOS) of HBTA at 0 and 25 GPa. The top of the valence band is mainly due to the contribution of p states of N1, N3 and N5 atoms, while N2 and N3 atoms dominates the bottom of conduction band with very less contribution arising from p states of N1 and N4 atoms. There is a strong hybridization between p states of nitrogen atoms and s states of carbon atom in the energy range from -8 to -9 eV. Similarly, s states of hydrogen and carbon atoms, p states of nitrogen (N4 and N5) atoms overlap with each other at -10 to -11 eV. The calculated band gap at 0 GPa using TB-mBJ potential is found to be an indirect band gap of 4.31 eV along $\Gamma - Z$ direction. The effect of pressure shifts
the conduction bands towards lower energies leading to a reduction in the band gap by 21.7% at 25 GPa. The pressure induced lowering of band gap is also observed in other energetic materials like RDX[19], octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)[20] and nitromethane[21], which quantitatively agrees with our results. Moreover, the peaks in DOS gradually becomes wider at elevated pressure and shift towards lower energy region leading to an increase in the band dispersion. This suggests the sensitivity of valence electrons to the external pressure.

![DOS plots](image)

**Figure 3.** Calculated partial density of states of HBTA using TB-mBJ potential at (a) 0 GPa and (b) 25 GPa.

5. Hirshfeld analysis

Hirshfeld surface analysis is one of the emerging tools for exploring the nature of intermolecular interactions within the crystal. It helps us to study the surface features of various types of intermolecular contacts and these features can be identified by calculating normalized contact distance ($d_{\text{norm}}$) based on $d_i$, $d_e$ and van der Waals (vdW) radii of the atoms[22], which is given by the following equation:

$$d_{\text{norm}} = \frac{(d_i - r_{i_{\text{vdW}}})}{r_i} + \frac{(d_e - r_{e_{\text{vdW}}})}{r_e}$$

Where $r_i$ and $r_e$ are the vdW radii of the particular atoms which are inside and outside to the surfaces, respectively. The Hirshfeld surfaces mapped over $d_{\text{norm}}$ are characterized by red-white-blue regions: closer contacts (negative $d_{\text{norm}}$ value), vdW contacts (zero $d_{\text{norm}}$ value) and longer contacts (positive $d_{\text{norm}}$ value), respectively. In addition, the 3D Hirshfeld surfaces were minimised into 2D fingerprint plots with specific atom...atom interactions that are experienced by the crystal[23], which provides a better interpretation regarding the types of intermolecular interactions present in the system.

The Hirshfeld surfaces and 2D fingerprint plots of HBTA crystal as a function of pressure are shown in the Figure 4. The dark red spots on the surface of HBTA corresponds to shorter contacts, i.e., the N4-H4...N2 and N5-H5...N1 hydrogen bonds, while blue region arises from long interactions (see Figure 4a). As pressure increases, more red spots are observed on the surface.
Figure 4. (a and g) Hirshfeld surfaces mapped over \( d_{\text{norm}} \), ((b-f) and (h-l)) fingerprint plots of HBTA broken down into specific pairs of atom types at 0 GPa and 25 GPa, respectively. The grey shadow represents the outline of the full fingerprint plot.

with very few blue region as shown in Figure 4g. This represents the general tendency of contacts shortening under pressure. The N...H/H...N interactions are the major contribution in the crystal structure that are represented by two discrete sharp spikes in the 2D fingerprint plots. These
N...H (37.0%) and H...N (29.1%) interactions do not show similar proportion to the Hirshfeld surfaces, which are visualized as a deep red spots on the d_{norm} surfaces by providing quantitative information on noncovalent hydrogen bonding interactions. The remaining contributions comes from N...N (18.7%), N...C/C...N (9.7%) and H...H (4.7%) interactions. The effect of pressure reduces the N...H/H...N contributions from 66.1% to 59.1% at 25 GPa. This represents the weakening of hydrogen bonding under pressure, which is in accord with the experimental results.

6. Conclusions
In summary, we have performed DFT calculations to study the structural and electronic properties of HBTA as a function of pressure up to 25 GPa. The obtained theoretical lattice constants and volume using optB88-vdW method are in good agreement with the experimental values under the studied pressure range. The effect of hydrostatic pressure on the crystal show the anisotropic compressibility in the lattice constants. The calculated bulk modulus (B_0) and its pressure derivatives (B'_0) are found to be 27.78 GPa and 5.82, respectively. The predicted electronic structure using TB-mBJ potential show that HBTA is an indirect band gap insulator and the band gap found to decrease gradually with increasing pressure (0 GPa = 4.31 eV, 25 GPa = 3.38 eV). The breakdown of Hirshfeld surfaces under pressure show reduction in the N...H/H...N contribution leading to hydrogen bond weakening.

7. Acknowledgments
BMA would like to thank Defense Research and Development Organization (DRDO) through ACRHEM for the financial support under grant No. DRDO/18/1801/2016/01038:ACREHM-PHASE-III, and the CMSD, University of Hyderabad, for providing computational facilities.

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