High-Pressure Studies of Hydrogen-Bonded Energetic Material 3,6-Dihydrazino-s-tetrazine Using DFT

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ABSTRACT: Hydrogen bonding is an important non-covalent interaction that plays a key role in most of the CHNO-based energetic materials, which has a great impact on the structural, stability, and vibrational properties. By analyzing the structural changes, IR spectra, and the Hirshfeld surfaces, we investigated the high-pressure behavior of 3,6-dihydrazino-s-tetrazine (DHT) to provide detailed description of hydrogen bonding interactions using dispersion-corrected density functional theory. The strengthening of hydrogen bonding is observed by the pressure-induced weakening of covalent N–H bonds, which is consistent with the red shift of NH/NH₂ stretching vibrational modes. The intermolecular interactions in DHT crystals lead to more compact and stable structures that can increase the density but diminish the heat of detonation, Q. The calculated detonation properties of DHT (D = 7.62 km/s, P = 25.19 GPa) are slightly smaller than those of a similar explosive 3,6-bis-nitroguanyl-1,2,4,5-tetrazine (D = 7.9 km/s, P = 27.36 GPa). Overall, the crystallographic and spectroscopic results along with Hirshfeld surface analysis as a function of pressure reveal the presence of strong hydrogen bonding networks in the crystal structure of DHT.

1. INTRODUCTION
In the world of advanced technology, researchers are still digging deep down the track to obtain the balance between high performance and good molecular stability in order to design high-energy-density materials. However, the major goal in the field of energetic materials is to develop more powerful and insensitive explosives, propellants, pyrotechnics, and oxidizers. To construct these types of explosives, many factors need to be considered (e.g., safety, energy, cost, etc.) before they are applied for practical applications. One among such parameters is sensitivity, which is a major problem of energetic materials and has to be taken into account during production, storage, and transportation. The best approach to improve the performance of an explosive without compromising safety is to choose the material that can form hydrogen bonding networks. These noncovalent interactions, especially hydrogen bonding interactions, have a remarkable influence on the physical and chemical properties of explosives giving rise to efficient packing in the crystal, which in turn improves the density and stability of the material. In addition, the low solubility in water is an extra advantage for strongly bonded energetic materials, which can provide better sensitivity together with low toxicity. Various hydrogen-bonded energetic materials have been extensively studied in the recent years to understand the nature of intermolecular iterations. For instance, the strong hydrogen bonding networks in 2,4,6-trinitro-1,3,5-benzenetriamine (TATB) not only enable higher density (ρ = 1.937 g/cm³) but also are responsible for its insolvibility in most of the common solvents. Recently synthesized ecofriendly energetic material hydrazine 5,5'-bitetrazole-1,1'-diloylate (HA·BTO) exhibits higher crystal density (ρ = 1.913 g/cm³) than that of 1,3,5-trinitro-1,3,5-triazinan (RDX, ρ = 1.806 g/cm³) due to the influence of strong hydrogen bonding networks. The huge number of intermolecular hydrogen bonds not only play a crucial role in the formation of an interesting structure but also improve the stability of HA·BTO. Our previous results also showed that the presence of strong hydrogen bonding in ammonium dinitramide (ADN) is responsible for more hygroscopic nature than that of ammonium perchlorate (AP).

Pressure on the scale of gigapascals can cause remarkable changes in the intermolecular interactions and reveals the hidden phenomena lying behind the extreme conditions. Moreover, the effect of pressure on the crystal structure of energetic materials can facilitate an efficient crystal packing and tune the noncovalent hydrogen bond interactions, thereby improving the detonation properties. These types of studies provide a better understanding about the nature of hydrogen bonding and structural stability of the energetic materials under pressure. Li et al. carried out high-pressure studies on energetic material aci-amidinium nitrate (C₃N₆H₆·NO₃⁻) using a diamond anvil cell. Their results show a deviation in the ideal hydrogen-bonded arrays along with a small slippage between adjacent ion pairs, which is responsible for the fabrication of new high-energy-density materials for better detonation performance. The pressure-induced rearrangement

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of hydrogen-bonded networks causes a phase transition in the carbohydrazide (CON\(_4\)H\(_6\)) energetic material.\(^{17}\) The reported high-pressure phase with space group \(P\bar{1}\) exhibits almost 23.1% higher density than that of the ambient structure (\(P21/n\)). However, the influence of pressure can change the direction of atoms and molecules in hydrogen-bonded structures, allowing the explosive properties (such as sensitivity) to be modified. Therefore, it is particularly interesting to study the high-pressure behavior of hydrogen-bonded systems for exploring high-energy-density materials.

Nitrogen-rich energetic materials, especially tetrazine-based compounds, have attracted special attention due to their high positive heat of formation (HOF), higher densities, and better oxygen balance (OB).\(^{18}\) As a component of gun and rocket propellant,\(^{19}\) ecofriendly smoke ingredient of pyrotechnic composition, 3,6-dihydrazino-s-tetrazine (DHT) is considered to be a nitrogen-rich energetic material with the measured HOF and \(H_{\text{fl}}\) values of +536 kJ/mol and 65 cm (2.5 kg, type 12), respectively.\(^{19}\) It can detonate with a rate of 7.54 km/s in the unconfined pressed pellets of 0.50 in. in diameter. The carbon-free combustion and hot flames of DHT have made it an ideal for the new-generation ecofriendly firework.\(^{20}\)

Furthermore, it has been used to design a variety of other nitrogen-rich energetic materials, such as 3,6-di-azido-1,2,4,5-tetrazine.\(^{21}\) DHT was first synthesized by Hiskey et al. in 1990,\(^{22,23}\) and later recognized by several experimental groups,\(^{24–29}\) but very few theoretical studies were reported.\(^{30–33}\) Hu et al. studied the intermolecular interactions of DHT using computational modeling and found that the strong intermolecular hydrogen bonding networks dominantly contributed to the dimers.\(^{33}\) Consequently, the variations identified on a microscopic level can also affect the macroscopic properties like density, which may further improve the performance of an explosive. Therefore, the increase in density of DHT under pressure may greatly influence the detonation properties and applications. Herein, we report the high-pressure investigation of structural and vibrational properties of DHT using first-principles calculations. Its axial and bond compressibilities and pressure-volume equation of state have been calculated. In addition, the effect of pressure on NH/NH\(_2\) stretching frequencies is crucial in understanding the behavior of hydrogen bonding. More information about the variations in packing patterns were obtained from Hirshfeld surfaces and the fingerprint plots. The present study explores the pressure-induced changes in intermolecular interactions to provide valuable information about the stability of hydrogen-bonded energetic materials.

2. RESULTS AND DISCUSSION

2.1. Structural Properties. DHT crystallizes in the monoclinic \(P21/c\) symmetry with lattice parameters \(a = 4.043 \text{ Å}, b = 5.644 \text{ Å}, c = 12.129 \text{ Å}, \beta = 99.124^\circ\), and \(Z = 2\) at 173 K.\(^{19}\) The molecular geometry and crystal structure of DHT are presented in Figures 1 and 2, where the nitrogen atoms attached to the hydrazino group and the tetrazine ring are nearly coplanar with an axial symmetry. Each molecule in the crystal structure connects with the neighboring molecules to form three-dimensional \(\text{N–H···N}\) hydrogen bonding networks in the form of herringbone-like pattern. The presence of 12 hydrogen bonds in each molecule can strengthen the stability of the compound. The relaxed lattice parameters and the optimized volume obtained using various exchange–correlation functionals are presented in Table 1 along with the experimental values. It is found that the calculated lattice parameters using local-density approximation (LDA) are smaller than the experimental results, whereas the generalized gradient approximation (GGA) values are overestimated. The well-known tendency of LDA/GGA calculations to underestimate/overestimate the lattice constants is precisely reflected in the obtained volumes (242.5/320.3), which fall below/above the experimentally measured volume of 272.9, respectively. In contrast, the correction to the Perdew–Burke–Ernzerhof (PBE) functional (TS and D2) provides reasonable improvement with small deviations when compared with experimental unit cell parameters. Especially, by the TS method, the error in the calculated volume is reduced to 0.01%, indicating the necessity of van der Waals (vdW) interactions while studying the structure of a DHT crystal.

To understand the origin of the response of DHT as a function of pressure, we carried out a detailed investigation of its crystal structure at different pressures up to 30 GPa in a step...
size of 5 GPa at 0 K. Remarkably, DHT exhibits anisotropic behavior along three crystallographic directions under pressure (see Figure 3a). The compressibility in the \( a \)-direction is markedly greater than that in the \( b \)- and \( c \)-directions. At 30 GPa, lattice parameters \( a \) and \( b \) decrease by 28.6 and 8.17%, respectively, whereas \( c \) first increases and then slightly decreases by 0.17% from its ambient pressure value. This indicates that the structure of DHT is much softer in the \( a \)-axis than in the \( b \)- and \( c \)-directions. Furthermore, as pressure increases, the unit cell volume decreases monotonically and reaches 85% of its ambient volume by 30 GPa (Figure 3c), which in turn enhances the density from 1.72 to 2.67 g/cm\(^3\). The resulting \( P-V \) data is used to calculate the bulk modulus \( (B_0) \) and its pressure derivatives \( (B_0)' \) by fitting with the third-order Birch Murnaghan equation of state.

Figure 3. Calculated pressure dependence of (a) unit cell parameters \((a, b, c)\), (b) normalized unit cell parameters \((a/a_0, b/b_0, c/c_0)\), (c) volume \((V)\), and (d) normalized volume \((V/V_0)\) of DHT. The solid red line represents the compression data fit to the third-order Birch Murnaghan equation of state.

Table 1. Calculated Lattice Parameters \((a, b, c \text{ in } \text{Å})\), Lattice Angle \((\beta \text{, in Degrees})\), and Volume \((V \text{ in } \text{Å}^3)\) of DHT Using PBE-GGA and Dispersion-Corrected (TS, D2) Functionals Along with Experimental Data\(^{49,50}\,

|          | LDA       | PBE       | TS        | D2        | exp'\(^{49}\) |
|----------|-----------|-----------|-----------|-----------|--------------|
| \( a \)  | 3.996 (−1.18%) | 4.798 (+18.64%) | 4.178 (+3.31%) | 4.036 (−0.17%) | 4.043        |
| \( b \)  | 5.364 (−4.97%) | 5.340 (−5.39%) | 5.506 (−2.45%) | 5.541 (−1.83%) | 5.644        |
| \( c \)  | 11.532 (−4.92%) | 12.501 (+3.06%) | 11.984 (−1.19%) | 11.855 (−2.25%) | 12.129       |
| \( \beta \)| 101.23 (+2.12%) | 88.9 (−10.31%) | 98.22 (−0.9%) | 99.9 (0.78%) | 99.12        |
| \( V \)  | 242.51 (−11.31%) | 320.32 (17.37%) | 272.95 (0.01%) | 261.19 (4.29%) | 272.91       |

“*The relative errors (in percentage) with respect to experiments are given in parentheses; here, ‘+’ and ‘−’ signs indicate overestimation and underestimation of the calculated values, respectively, when compared with experiments.
three N–H bonds of the DHT molecule points to the three neighboring molecules. These intermolecular hydrogen bond distances can be measured using the N···H distance. For instance, DHT molecule connects with neighboring molecules in the direction of N1, N2, and N4 atoms and the corresponding N···H distances are 2.157, 2.166, and 1.872 Å, respectively. The average distances of the intermolecular N···H pairs and N–H covalent bonds are 2.06 and 1.04 Å, respectively. These hydrogen bonds exhibit vast changes in the bond strength as a function of pressure. The calculated pressure dependence of the intramolecular N–H (dN–H) bond length, intermolecular N···H (dN···H) and N···N (dN···N) distances, and N–H···N (∠N–H···N) bond angles are shown in Figure 4. The obtained N–H bond lengths show anisotropic behavior as a function of pressure. The calculated pressure dependence of the intramolecular N–H (dN–H) bond length, intermolecular N···H (dN···H) and N···N (dN···N) distances, and N–H···N (∠N–H···N) bond angles are shown in Figure 4. The obtained N–H bond lengths show anisotropic behavior as a function of pressure (see Figure 4a); especially, the covalent N3–H3 bond length is enlarged and increased from 1.044 Å at 0 GPa to 1.111 Å at 30 GPa. The increase of the dN–H bond length represents the weakening of covalent N–H bonds by facilitating the release of hydrogen atom. In general, the N–H covalent bond becomes larger under compression, whereas the H···N interaction shrinks due to reducing repulsive force, leading to shortening of the total N–N distance. From Figure 4b, the average distances between the intermolecular N–H contacts at 0 GPa (2.06 Å) and 30 GPa (1.97 Å) are found to be less than the sum of the vdW radii of H and N (2.7), which supports the strengthening of hydrogen bond due to shortening of intermolecular N–H contact distance under pressure. The fundamental criteria to determine the strengthening or/and weakening of hydrogen bonding mainly depend on the above analyzed intermolecular distance and the frequency of the corresponding vibrational stretching modes, which will be discussed in the next section.

2.2. Vibrational Properties. The vibrational spectroscopy study of hydrogen-bonded energetic materials under compression can tune the range of frequencies due to weak intermolecular interactions and explains the effect of hydrogen bonding on the stability of crystal structure. Usually, the weakening or strengthening of hydrogen bonds can be visualized based on the shift in the D–H vibrational frequency. For any material containing D–H···A hydrogen bonds (D and A represent donor and acceptor, respectively), the IR spectra corresponding to a particular frequency shift toward lower energies by decreasing the D–A distance. This can be explained in terms of electrostatic attraction between the proton and acceptor atom. When a system is compressed, the distance between the donor and acceptor atoms reduces, enhancing the electrostatic attraction between H and A. This leads to lengthening of D–H bond distance by reducing the D–H stretching frequencies toward lower energies. This is in accord with the aforementioned N–H bond length, where the
H···N distance decreases as a function of pressure, which strengthens the hydrogen bonding. As discussed above, DHT crystallizes in the monoclinic structure containing 32 atoms in the primitive cell, resulting in 96 vibrational modes. From the group analysis of the P21/c space group, the representation of symmetry decomposition is

\[ \Gamma_{\text{tot}} = 24A_u \oplus 24B_u \oplus 24A_g \oplus 24B_g \]

with three acoustic modes

\[ \Gamma_{\text{acoustic}} = A_u \oplus 2B_u \text{ and } 93 \text{ optical modes} \]

\[ \Gamma_{\text{optical}} = 23A_u \oplus 22B_u \oplus 24A_g \oplus 24B_g \]

Group theoretical analysis of 93 optical modes shows that 24A_u \oplus 24B_u are Raman-active modes and 23A_u \oplus 22B_u are IR-active modes. The obtained optical modes along with corresponding vibrational assignments are presented in Table 2. Of these 93 optical modes, 18 were under the frequency of 300 cm\(^{-1}\). However, in remaining 75 modes, 24 pairs of modes (48 modes) were under 10 cm\(^{-1}\) from each other (15 pairs of the 24 were below 5 cm\(^{-1}\) and 9 of the 24 were below 3 cm\(^{-1}\)). The pressure-induced IR spectral variations of DHT in the frequency range of 70–470, 465–655, 750–1435, 1420–1680, and 1800–3300 cm\(^{-1}\) are presented in Figure 5. The lattice modes between the vibrational frequencies of 58 and 322 cm\(^{-1}\) are mainly due to translational and/or rotational motion of the tetrazine ring and the NH\(_2\) group. As pressure increases, lattice modes shift monotonically toward higher frequencies due to the reduction of intermolecular separation, which results in strengthening of interactions between adjacent molecules.\(^{32,53}\)

Table 2. Calculated Phonon Frequencies Along with the Corresponding Assignment of DHT at the DFT–TS Equilibrium Volume Using the Norm–Conserving Pseudopotentials (NCP) Approach under Ambient Pressure

| mode     | frequency (cm\(^{-1}\)) | assignment |
|----------|-------------------------|------------|
| M4–M22  | 58–322                  | lattice modes |
| M23, M24| 364–365                 | ring libr  |
| M25–M28 | 374–463                 | ring libr, NH\(_2\) rot |
| M29     | 477                     | NH\(_2\) rot |
| M30, M31| 480–490                 | NH\(_2\) wagg |
| M32–M34 | 496–526                 | NH\(_2\) rot |
| M35     | 527                     | NH\(_2\) bend, N–C=\(\equiv\)N wagg |
| M36     | 544                     | NH\(_2\) rot |
| M37, M38| 636–642                 | ring breath |
| M39, M40| 665–686                 | ring bend, NH\(_2\) wagg |
| M41–M44 | 763–802                 | NH wagg    |
| M45     | 809                     | NH\(_2\) wagg, NH str |
| M46     | 813                     | NH wagg    |
| M47     | 845                     | ring breath |
| M48–M50 | 846–869                 | NH rock    |
| M51–M58 | 987–1074                | NH\(_2\) wagg, C–N, C=\(\equiv\)N, N–N str |
| M59–M62 | 1157–1178               | NH\(_2\) wagg |
| M63, M64| 1269–1274               | N–C=\(\equiv\)N asy str, NH\(_2\) twist |
| M65–M68 | 1284–1292               | NH\(_2\) twist |
| M69, M70| 1330–1335               | NH bend    |
| M71, M72| 1379.02–1379.77         | C–N, C=\(\equiv\)N str, NH bend |
| M73–M80 | 1444–1557               | NH bend |
| M81–M84 | 1648–1659               | NH\(_2\), NH scissor |
| M85–M88 | 2966–3064               | NH str      |
| M89–M92 | 3211–3215               | NH\(_2\) sym str |
| M93–M96 | 3271.49–3271.78         | NH\(_2\) asym str |

300 cm\(^{-1}\). However, in remaining 75 modes, 24 pairs of modes (48 modes) were under 10 cm\(^{-1}\) from each other (15 pairs of the 24 were below 5 cm\(^{-1}\) and 9 of the 24 were below 3 cm\(^{-1}\)). The pressure-induced IR spectral variations of DHT in the frequency range of 70–470, 465–655, 750–1435, 1420–1680, and 1800–3300 cm\(^{-1}\) are presented in Figure 5. The lattice modes between the vibrational frequencies of 58 and 322 cm\(^{-1}\) are mainly due to translational and/or rotational motion of the tetrazine ring and the NH\(_2\) group. As pressure increases, lattice modes shift monotonically toward higher frequencies due to the reduction of intermolecular separation, which results in strengthening of interactions between adjacent molecules.\(^{32,53}\)

Figure 5b shows the rotation and bending modes of the NH\(_2\) group and bending and breathing modes of the tetrazine ring, whereas NH (wagging, stretching, rocking, and bending); NH\(_2\) (wagging and twisting); ring breathing; and C–N, C=\(\equiv\)N, and N–N stretching modes are shown in the Figure 5c. These modes display a blue shift up to the studied pressure range. The most pronounced one is the significant splitting of the NH bending mode (1550 cm\(^{-1}\)) into two distinguishable bands at around 20 GPa (see Figure 5d). One of these modes shows a negative pressure dependence, whereas the other displays a positive dependence.

The application of pressure to N–H stretching modes provides a vital information regarding the variations in hydrogen bonding networks. As shown in Figure 5ef, the N–H stretching bands located between 2950 and 3300 cm\(^{-1}\) are composed of three modes: the highest-intensity mode at 2986 cm\(^{-1}\) is assigned to the stretching of the NH group. Further, the peaks at 3215 and 3271 cm\(^{-1}\) correspond to the symmetric and asymmetric stretching modes of the NH\(_2\) group (see Figure 6), respectively. In contrast to other bands, the two lowest-frequency modes located at 2986 and 3215 cm\(^{-1}\) move toward lower frequencies with increasing intensities as a function of pressure. The highest-frequency mode appears to reduce and eventually disappears at the maximum pressure of 30 GPa. The frequency lowering is more pronounced in the NH and NH\(_2\) symmetric stretching groups than in the NH\(_2\) asymmetric stretching mode. The observed decreasing activity in NH/NH\(_2\) vibrational modes agrees with generalized rules of pressure-induced strengthening of N–H···N hydrogen bonding in the DHT crystal. As shown in Figure 2, the N–H groups of various molecules serve as proton donors and nitrogen atoms in the tetrazene ring act as proton acceptors to form hydrogen bonding networks. The adoption of pressure will reduce the N–H···N hydrogen bond lengths and the separation between neighboring molecules along hydrogen-bonded chains. The observed variation trends of NH/NH\(_2\) vibrational modes as a function of pressure are quantitatively similar to those in the previous studies of hydrogen-bonded energetic materials.\(^{54}\)

2.3. Hirshfeld Analysis. The Hirshfeld surface analysis has made it possible to explore the nature of intermolecular interactions that can provide a direct insight into the molecular crystal. Recently, Ma and his co-workers\(^{55}\) used the Hirshfeld surface theory to study the intermolecular interactions of 10 existing impact-sensitive highly energetic (SHE) materials including RDX, 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), CL-20, and octanitrocubane. Subsequently, they found that the covalent O···O interactions are the predominant intermolecular interactions in SHE, whereas less sensitive highly energetic materials (LSHE) are governed by intermolecular hydrogen bonding. The lack of intermolecular hydrogen bonding networks and planar big \(\pi\)-conjugated molecular geometric structures in SHE crystals are responsible for their low molecular stability when compared to that of LSHE. They also reported that the intermolecular O···O interactions in SHE can break more readily and thus are more sensitive compared with LSHE.

To have a clear visualization of the molecule, the Hirshfeld surfaces were shown in a transparent mode. The strong N···H–N hydrogen bonding networks between the respective donor and acceptor atoms are seen as deep red spots on the Hirshfeld surfaces mapped over \(\rho_{\text{norm}}\) (see Figure 7a).
N1, and N4–H4B···N2 hydrogen bonds. These observations are further confirmed by the electrostatic potential (see Figure 7b) mapped on Hirshfeld surfaces that clearly demonstrates the presence of an electropositive (blue) region around hydrogen atoms, whereas a strong negative electrostatic potential (red) surrounding the nitrogen atoms. Furthermore, the breakdown of the fingerprint plot into specific atom types reveals that 58.3% of the total Hirshfeld surfaces are due to N···H/H···N interactions, which appear as a pair of distinct sharp spikes in the bottom left/right region of the two-dimensional (2D) fingerprint plot, representing the characteristics of strong hydrogen bonding. The participation of H···H contacts is shown in the middle region of the fingerprint plot with overall 26.3% of the Hirshfeld surfaces (see Figure 8a,b).

As pressure increases, the blue region decreases and becomes almost invisible at 30 GPa (see Figure 8c,d). However, the red region spreads all over the Hirshfeld surfaces, indicating an increase in the number of closer contacts under pressure. In general, the pressure-induced variations in the intermolecular interactions will tend to bring the molecules together, enabling a denser molecular packing. However, the structure of fingerprint has been compressed and drawn toward the origin due to shortening of longer intermolecular contacts, which is related to the decrease of $d_e$ value at elevated pressures (0 GPa = 1.54 Å; 30 GPa = 1.26 Å). Furthermore, the orange and red points in the fingerprint plots of 30 GPa indicate the closest contacts in this crystal structure. Overall, the applied pressure increases the

Figure 5. Calculated IR spectra in the frequency range of (a) 70–470 cm$^{-1}$, (b) 465–655 cm$^{-1}$, (c) 750–1435 cm$^{-1}$, (d) 1420–1680 cm$^{-1}$, (e) 1800–3030 cm$^{-1}$, and (f) 3010–3300 cm$^{-1}$ of DHT as a function of pressure.
contribution of N···H/H···N and N···N interactions whereas decreases the H···H interactions to the total Hirshfeld surfaces (see Figure 9).

2.4. Detonation Properties. The performance of explosives is exclusively determined by their detonation properties: the higher the detonation velocity and pressure, the greater the detonation performance. These detonation characteristics can be calculated using various computer codes through density and HOF. Foremost, the condensed phase HOF of C
$_a$H$_b$N$_c$O$_d$-based explosives can be predicted by the following equation:

$$
\Delta_f H^\theta(c) = \Delta_f H^\theta_{EC} + 105.0\Delta_f H^\theta_{IEC} - 106.6\Delta_f H^\theta_{DEC}
$$

(1)

where $\Delta_f H^\theta(c)$ is the condensed phase HOF (kJ/mol) and $\Delta_f H^\theta_{IEC}$ and $\Delta_f H^\theta_{DEC}$ are the increasing and decreasing energy content parameters of an explosive, respectively. From eqs 1 and 2, the value of $\Delta_f H^\theta(c)$ can be increased by adding more number of carbon and nitrogen atoms as well as by reducing the number of hydrogen and oxygen atoms. However, the calculated $\Delta_f H^\theta(c)$ value for DHT (+501.7 kJ/mol) is found to be higher than that for BNT (+336.1 kJ/mol) due to the absence of oxygen atoms in the former. Subsequently, the obtained crystal density and HOF were used to predict the detonation characteristics through Kamlet–Jacobs equations:

$$
\Delta_f H^\theta_{EC} = 32.33a - 39.49b + 92.41c - 63.85d
$$

(2)

Figure 6. Few simulated vibrational modes of the DHT crystal.

Figure 7. (a) Hirshfeld surface of the DHT crystal for visualizing the intermolecular interactions. (b) Electrostatic potential mapped on the Hirshfeld surface. The green dashed lines represent the hydrogen bonds.
$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho)$  

\(P = 1.558 NM^{1/2}Q^{1/2}/\rho\)\(^2\)

where \(D\) and \(P\) are the detonation velocity (km/s) and detonation pressure (GPa), respectively, which can be determined by substituting \(\rho\), the crystal density (g/cm\(^3\)); \(M\), the average molecular weight of gaseous products (g/mol); \(N\), the moles of detonation gas products per gram of explosive; and \(Q\), the heat of detonation (cal/g) values according to the largest exothermic principle.\(^5^9\) Furthermore, the sensitivity and performance of an explosive can be roughly predicted by computing the oxygen balance (OB) using the following formula\(^6^0\)

\[\text{OB} = \frac{- (2a + 0.5 \times b - c)}{M} \times 1600\]

where \(M\) represents the molecular weight and \(a\), \(b\), and \(c\) are the number of C, H, and O atoms, respectively. Generally, the higher OB leads to greater detonation pressure and velocity and thus superior performance of an explosive.\(^6^1\) At the same time, the negative OB can also be used to predict the shock sensitivity, where the energetic materials with zero oxygen balance are highly sensitive to shock.\(^6^2\) The calculated HOF, \(Q\), \(D\), and OB of DHT along with BNT are presented in Table 3. Moreover, the detonation characteristics of DHT (\(D = 7.62\) km/s, \(P = 25.19\) GPa) are smaller than those of BNT (\(D = 7.9\) km/s, \(P = 27.36\) GPa). This inadequacy in the
performance is due to negative OB of DHT that may significantly reduce the amount of velocity and pressure released during detonation. The negative oxygen balance also indicates that DHT is less sensitive than BNT. It is worth noting that the heat of detonation \( Q \) for DHT is less than that for BNT. The hydrogen-bonded N−H···N intermolecular interactions serve as a stabilizing factor that reduces the heat of detonation, \( Q \).

3. CONCLUSIONS

In summary, we have systematically investigated the structural and vibrational properties of a hydrogen-bonded energetic material 3,6-dihydrazino-s-tetrazine (DHT) under high-pressure up to 30 GPa via dispersion-corrected DFT. The obtained ground-state properties using standard exchange–correlation functionals (LDA/GGA) show drastic variations from experimental values, whereas the vdW-TS method provides an accurate description of the intermolecular interactions for the DHT crystal. The linear compressibility curves along the crystallographic \( a \)- and \( c \)-axes are shown to be the most and least compressible, respectively. The predicted bulk modulus values reveal that DHT is more harder than the well-known energetic oxidizers ammonium dinitramide (ADN) and ammonium perchlorate (AP). The existence of strong hydrogen bonding networks in the high-pressure region weakens the covalent N−H bond lengths, which is consistent with the decreasing activity of NH/NH\(_2\) stretching vibrational modes. The 2D fingerprint plots reveal that 58.3% of the total Hirshfeld surfaces are due to N···H/H···N interactions, indicating the significance of hydrogen bonds as primary intermolecular interactions in the DHT crystal. The calculated heat of formation (+501.7 kJ/mol) and detonation properties \( (D = 7.62 \text{ km/s}, P = 25.19 \text{ GPa}) \) of DHT are found to be higher and slightly smaller, respectively, than those of the similar explosive BNT.

4. COMPUTATIONAL DETAILS

All calculations were performed using the plane-wave pseudopotential method based on DFT, which is implemented through the Cambridge Series of Total Energy Package.34,35 The exchange–correlation potentials were described within the generalized gradient approximation (GGA) by the Perdew–Burke–Ernzerhof (PBE) functional.36 The Broyden–Fletcher–Goldfarb–Shanno (BFGS) optimization scheme37 was used to obtain the equilibrium crystal structure. The ultrasoft pseudopotentials (USP) have been utilized to calculate the structural properties, whereas norm-conserving pseudopotentials (NCP) for obtaining zone-center IR spectra of DHT under pressure up to 30 GPa. The plane-wave cut-off energies of 600 eV for USP and 950 eV for NCP were used to expand the wave functions. A 6 × 5 × 2 Monkhorst–Pack grid38 was used for Brillouin zone integration. The self-consistent energy convergence criterion was set to \( 5.0 \times 10^{-6} \) eV/atom, and the force per atom diminished to 0.01 eV/Å. The maximum stress and displacement were set to 0.02 GPa and \( 5.0 \times 10^{-4} \) Å, respectively. The vibrational spectra of DHT were calculated using the linear response method as implemented in density functional perturbation theory.

The accurate description of weak intermolecular interactions (e.g., hydrogen bonding, van der Waals (vdW) forces) has been the subject of interest from many decades. The conventional exchange–correlation functionals (e.g., LDA, GGA) in DFT are unable to accurately capture the long-range vdW forces. For instance, LDA underestimates the volume by 7−30%, whereas GGA overestimates by 10−15% for CL-20,40 RDX,40 HMX,41 PETN,42 TATB,43 FOX-7,44 and

![Figure 9. Pressure versus percentage contributions to the Hirshfeld surface area for the various intermolecular interactions of the DHT crystal.](image)

| Table 3. Calculated Detonation Properties of DHT Compared with the Values of 3,6-Bis-Nitroguanyl Tetrazine (BNT)56 |
|-------------|------------------|-----------------|-----------------|-----------------|------------------|
| \( \rho \) (g/cm\(^3\)) | HOF (kJ/mol) | \( Q \) (cal/g) | \( D \) (km/s) | \( P \) (GPa) | OB (%) |
| DHT (C\(_2\)H\(_6\)N\(_8\)) | 1.729 | 501.76 (536)\(^{19}\) | 1072.68 | 7.62 (7.54)\(^{19}\) | 25.19 | −78.80 |
| BNT (C\(_4\)H\(_6\)N\(_{10}\)O\(_4\)) | 1.76\(^{56}\) | 336.1 | 1165.61 | 7.90 | 27.36 | −55.78 |
TNAD. The inadequacies in describing the intermolecular interactions not only affect the prediction of accurate crystal geometry but also lead to errors in the computed properties such as density, elastic modulus, cohesive energy, and band gap. Recently, various improvements were made to extend standard DFT to include these types of weak dispersive forces. Particularly, the empirical vdW corrections such as the Grimme (DFT-D2) and Tkatchenko and Scheffler (DFT-TS) corrections to PBE are most successful methods. Within the DFT + D framework, the total energy including vdW correction is given by

\[ E_{\text{DFT+D}} = E_{\text{DFT}} + E_{\text{disp}} \]

where \( E_{\text{disp}} \) is the empirical dispersion correction computed as

\[ E_{\text{disp}} = -s_0 \sum_{i<j} \frac{C_{ij}}{R_{ij}^6} f_{\text{damp}}(R_{ij}) \]

where \( R_{ij}, C_{ij} \) and \( s_0 \) represent the interatomic distance, dispersion coefficient for the pair of \( i \text{th} \) and \( j \text{th} \) atoms, and a global scaling factor that only depends on the density functional used, respectively. The damping function, \( f_{\text{damp}} = \frac{1}{1 + e^{-a(R_{ij}-R_{c})}} \), is introduced to avoid divergence for small \( R_{ij} \).

The Hirshfeld surfaces of DHT were calculated using CrystalExplorer, which is a powerful tool for exploring the nature of intermolecular interactions within the crystal. The strength of the interactions can be described by \( d_{\text{norm}} \) (normalized contact distance)

\[ d_{\text{norm}} = \frac{(d_i - r_{i\text{vdw}})}{r_i} + \frac{(d_e - r_{e\text{vdw}})}{r_e} \]

where \( d_i \) and \( d_e \) denote the internal and external separations from the nearest atoms and \( r_i \) and \( r_e \) represent the vdW radii of the two atoms inside and outside the Hirshfeld surfaces. These close intermolecular contacts were identified by a three-dimensional \( d_{\text{norm}} \) surface in which the positive/negative values represent the intermolecular contacts that are longer/shorter than the vdW separations. The graphical plots are mapped onto the Hirshfeld surfaces with \( d_{\text{norm}} \) using red (shorter intermolecular contacts), white (contacts around the vdW separation), and blue (longer intermolecular contacts) colors. In addition, the 2D fingerprint plots associated with Hirshfeld surfaces can provide a summary of intermolecular interactions in the molecule.

**REFERENCES**

1. Gao, H.; Shreeve, J. M. Azole-based energetic salts. Chem. Rev. 2011, 111, 7377–7436.
2. Bemm, U.; Stmark, H. 1,1-Diamino-2,2-dinitroethylen: a novel energetic material with infinite layers in two dimensions. Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 1998, 54, 1997–1999.
3. Meng, L.; Lu, Z.; Ma, Y.; Xue, X.; Nie, F.; Zhang, C. Enhanced intermolecular hydrogen bonds facilitating the highly dense packing of energetic hydroxylammonium salts. Cryst. Growth Des. 2016, 16, 7231–7239.
4. Ye, C.; Shreeve, J. M. New atom/group volume additivity method to compensate for the impact of strong hydrogen bonding on densities of energetic materials. J. Chem. Eng. Data 2008, 53, 520–524.
5. Su, Z.; Liu, X.; Yang, Q.; Zhang, S.; Wei, Q.; Xie, G.; Chen, S.; Gao, S. Intermolecular interaction influenced energy and sensitivity of highly energetic salts: structure and physicochemical properties. CrystEngComm 2014, 16, 4245–4253.
6. Zhang, X.; Xiong, H.; Yang, H.; Cheng, G. Synthesis and detonation properties of S-Amino-2,4,6-trinitro-1,3-dihydroxy-benzene. ChemistryOpen 2017, 6, 447–451.
7. Yin, P.; Mitchell, L. A.; Parrish, D. A.; Shreeve, J. M. Comparative study of various pyrazole-based anions: A promising family of ionic derivatives as insensitive energetic materials. Chem. - Asian J. 2017, 12, 378–384.
8. Zhang, J.; Zhang, Q.; Vo, T. T.; Parrish, D. A.; Shreeve, J. M. Energetic salts with π-stacking and hydrogen-bonding interactions lead the way to future energetic materials. J. Am. Chem. Soc. 2015, 137, 1697–1704.
9. Foltz, M. F.; Ornellas, D. L.; Pagoria, P. F.; Mitchell, A. R. Recrystallization and solubility of 1,3,5-triamino-2,4,6-trinitrobenzene in dimethyl sulfoxide. J. Mater. Sci. 1996, 31, 1893–1901.
10. Zhang, Z. B.; Xu, C. X.; Yin, X.; Zhang, J. G. Hydrazine 5,5’-bitetrazole-1,1’-dioxide: a promising high density energetic salt with good properties. Dalton Trans. 2016, 45, 19043–19052.
11. Choi, C. S.; Prince, E. The crystal structure of cyclo-trimethylene-trinitramine. Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater. 1972, B28, 2857–2862.
12. Yedukondalu, N.; Vikas, D. G.; Vaitheeswaran, G. High pressure structural, elastic and vibrational properties of green energetic oxidizer ammonium dinitramide. J. Chem. Phys. 2016, 145, No. 064706.
13. Yan, T.; Li, S. R.; Wang, K.; Tan, X.; Jiang, Z. M.; Yang, K.; Liu, B. B.; Zou, G. T.; Zou, B. Pressure-induced phase transition in N–H···O hydrogen-bonded molecular crystal Oxamide. J. Phys. Chem. B 2012, 116, 9796–9802.
14. Sun, C. Q.; Zhang, X.; Zheng, W. The hidden force opposing ice compression. Chem. Sci. 2012, 3, 1455–1460.
15. Roszak, K.; Katrusiak, A. Giant anomalous strain between high-pressure phases and the mesomers of Urea. J. Phys. Chem. C 2017, 121, 778–784.
16. Li, S.; Li, Q.; Li, R.; Liu, J.; Yang, K.; Liu, B.; Zou, B. New assembly of acetamidinium nitrate modulated by high pressure. J. Phys. Chem. C 2014, 118, 23443–23450.
17. Yan, T.; Wang, K.; Tan, X.; Liu, J.; Liu, B.; Zou, B. Exploration of the hydrogen-bonded energetic material carboxyhydrate at high pressures. J. Phys. Chem. C 2014, 118, 22960–22967.
18. Chavez, D. E.; Hiskey, M. A.; Gilardi, R. D. 3,3’-Azobis(6-amino-1,2,4,5-tetrazine): a novel high-nitrogen energetic material. Angew. Chem., Int. Ed. 2000, 39, 1791–1793.
19. Hiskey, M. A.; Chavez, D. E.; Naud, D. L. Insensitive High-Nitrogen Compounds: Report LA-UR-01-1493 2001; Los Alamos National Laboratory, 2001; pp 1–10.
20. LoPresti, V. Versatile Explosives; Los Alamos Res Q, 2003; pp 4–12.
21. Li, X. T.; Pang, S. P.; Yu, Y. Z.; Luo, Y. Synthesis and theoretical studies of 3,6-diadido-1,2,4,5-tetrazine. Acta Chim. Sin. 2007, 65, 971.
(22) Chavez, D. E.; Hiskey, M. A. 1,2,4,5-Tetrazine based energetic materials. J. Energ. Mater. 1999, 17, 357–377.

(23) Chavez, D. E.; Hiskey, M. A. Synthesis of the bi-heterocyclic parent ring system 1,2,4-triazolo[4,3-b]1,2,4,5-tetrazine and some 3,6-disubstituted derivatives. J. Heterocycl. Chem. 1998, 35, 1329–1332.

(24) Oxley, J. C.; Smith, J. L.; Chen, H. Thermal decomposition of high-nitrogen energetic compounds-dihydrazido-s-tetrazine salts. Thermochim. Acta 2002, 384, 91–99.

(25) Saracoglu, N. Recent advances and applications in 1,2,4,5-tetrazine chemistry. Tetrahedron 2007, 63, 4199–4236.

(26) Pagoria, P. F.; Lee, G. S.; Mitchell, A. R.; Schmidt, R. D. A review of energetic materials synthesis. Thermochim. Acta 2002, 384, 187–204.

(27) Sysoev, A. V.; Moroshenkoa, Y. V.; Kolenoa, D. I. The interaction of 3,6-dihydrazino-s-tetrazine with some aliphatic aldehydes. Procedia Chem. 2014, 10, 467–472.

(28) Sinditskii, V. P.; Egorov, V. Y.; Rudakov, G. F.; Burzhava, A. V.; Filatov, S. A.; Sang, L. D. Thermal behavior and combustion mechanism of high-nitrogen energetic materials DHT and BATAz. Thermochim. Acta 2012, 535, 48–57.

(29) Talawar, M. B.; Sibalbanal, R.; Senthilkumar, N.; Prabhu, G.; Asthana, S. N. Synthesis, characterization and thermal studies on furazan and tetrazine-based high energy materials. J. Hazard. Mater. 2004, 113, 11–25.

(30) Jaidann, M.; Roy, S.; Rachid, H. A.; Lussier, L. S. A DFT theoretical study of heats of formation and detonation properties of nitrogen-rich explosives. J. Hazard. Mater. 2010, 176, 165–173.

(31) Roy, S.; Jaidann, M.; Ringquette, S.; Lussier, L. S.; Rachid, H. A. Predictions of thermodynamic properties of energetic materials using COSMO-RS. Procedia Comput. Sci. 2010, 1, 1203–1211.

(32) Lu, L.; Xu, K.; Zhang, H.; Wang, G.; Huang, J.; Wang, B.; Zhao, F. Structural and thermal characteristics of a high-nitrogen energetic material: G(AHDNE). Bull. Korean Chem. Soc. 2012, 33, 2325–2338.

(33) Hu, Y.; Ma, H. X.; Li, J. F.; Gao, R.; Song, J. R. Density functional theoretical study on intermolecular interactions of 3,6-disubstituted 1,2,4,5-tetrazines. Z. Naturforsch., B: J. Chem. Sci. 2013, 68, 1310–1320.

(34) Segall, M. D.; Lindon, P. J. D.; Probert, M. J.; Pickard, C. J.; Payne, M. C.; Teter, M. P.; Allen, D. C.; Arias, T. A.; Tkatchenko, A.; Scheffler, M. Accurate molecular van der Waals interactions from ground-state electron density and free-atom reference data. Phys. Rev. Lett. 2009, 102, No. 073005.

(35) Sinditskii, V. P.; Egorshev, V. Y.; Rudakov, G. F.; Burzhava, A. V.; Filatov, S. A.; Sang, L. D. Thermal behavior and combustion mechanism of high-nitrogen energetic materials DHT and BATAz. Thermochim. Acta 2012, 535, 48–57.

(36) Klapotke, T. M.; Preimesser, A.; Stierstorfer, J. Thermally stable 3,6-disubstituted 1,2,4,5-tetrazines. Z. Naturforsch., B: J. Chem. Sci. 2007, 63, e44–e45.

(37) Peiris, S. M.; Pangilinan, G. I.; Russell, T. P. Structural properties of ammonium perchlorate compressed to 5.6 GPa. J. Phys. Chem. A 2000, 104, 11188–11193.

(38) Goncharov, A. F.; Mana, M. R.; Zaj, J. M.; Gee, R. H.; Fried, L. E.; Montgomery, W. B. Polymerization of formic acid under high pressure. Phys. Rev. Lett. 2005, 94, No. 065505.

(39) Ciezak, J. A.; Jenkins, T. A.; Liu, Z.; Hemley, R. J. High-pressure vibrational spectroscopy of energetic materials: Hexahydro-1,3,5-trinitro-1,3,5-triazine. J. Phys. Chem. A 2007, 111, 59–63.

(40) Borstad, G. M.; Batyrev, I. G.; Jenkins, J. A. C. Cyanacetohydrazide under pressure: Chemical changes in a hydrogen-bonded material. J. Phys. Chem. A 2016, 120, 2712–2719.

(41) Ma, Y.; Zhang, A.; Xue, X.; Jiang, D.; Zhu, Y.; Zhang, C. Crystal packing of impact-sensitive high-energy explosives. Cryst. Growth Des. 2014, 14, 6101–6114.

(42) Chavez, D. E.; Hiskey, M. A.; Giraldi, R. D. Novel high-nitrogen materials based on nitroganyl-substituted tetrazines. Org. Lett. 2004, 6, 2889–2891.

(43) Keshavarz, M. H. Prediction of the condensed phase heat of formation of energetic compounds. J. Hazard. Mater. 2011, 190, 330–344.

(44) Camlet, M. J.; Jacobs, S. T. Chemistry of detonations. I. A simple method for calculating detonation properties of C-H-N-O explosives. J. Chem. Phys. 1968, 48, 23–35.

(45) Wang, G.; Gong, X.; Liu, Y.; Xiao, H. A theoretical investigation on the structures, densities, detonation properties, and pyrolysis mechanism of the nitro derivatives of phenols. Int. J. Quantum Chem. 2010, 110, 1691–1701.

(46) Throop, W. C.; Handrick, G. R. The relationship between performance and constitution of pure organic explosives. Chem. Rev. 1949, 44, 419–445.

(47) Wu, Q.; Zhu, W.; Xiao, H. A new design strategy for high-energy low-sensitivity explosives: combining oxygen balance equal to zero, a combination of nitro and amino groups, and N-oxide in one molecule of 1-amino-5-nitrotetrazole-3N-oxide. J. Mater. Chem. A 2014, 2, 13006–13015.

(48) Tamuliene, J.; Jonas, S.; Svajone, B. Influence of nitro group substitutes to the stability and energetic properties of N-(2,4,6-trinitrophenyl)-1H-1,2,4-triazole-3-amine. Am. J. Anal. Chem. 2017, 8, 125–141.

(49) Cady, H. H.; Larson, A. C. The crystal structure of 1,3,5-triamino-2,4,6-trinitrobenzene. Acta Crystallogr. 1965, 18, 485–496.
(64) Mayer, R.; Kohler, J.; Homburg, A. Explosives, 5th ed.; Wiley-VCH: Weinheim, 2002.
(65) Hall, T. N.; Holden, J. R. Navy Explosives Handbook, Explosion Effects and Properties—Part III, NSWC MP 88-116; White Oak Laboratory Naval Surface Warfare Centre, 1988.