

SUPPLEMENTARY INFORMATION for

# Cooperativity of Hydrogen Bonds in the Nitroamide Crystal: A Prototypical Case Study of Low-Sensitivity and High-Energy Explosives

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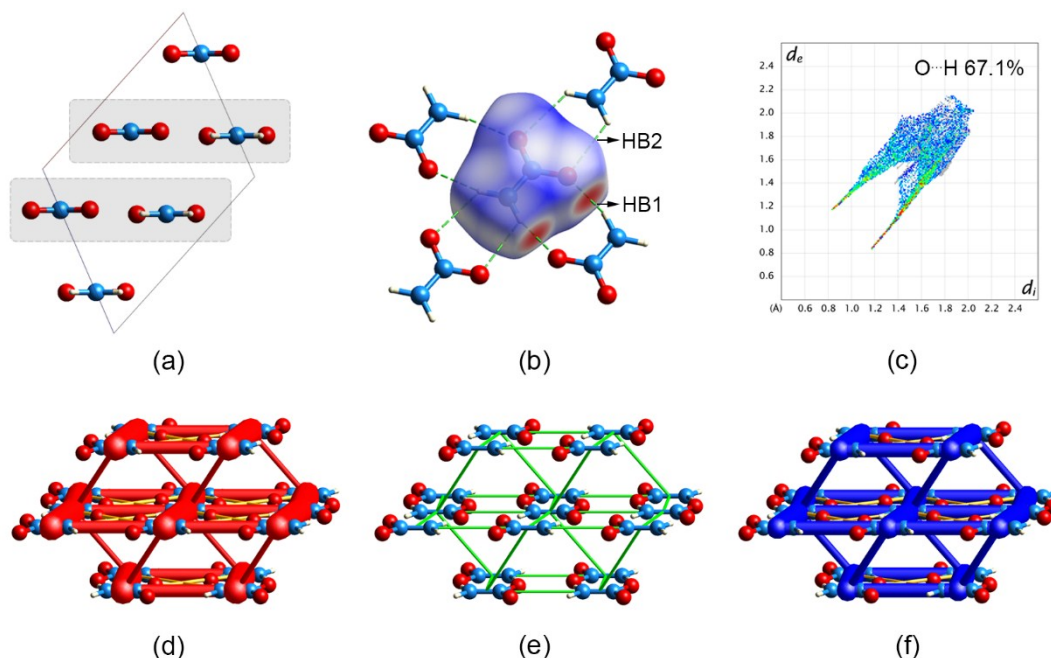
## 1. METHODS

**Hydrogen Bond Analysis.** The intermolecular hydrogen bonds (HBs) in the Nitroamide (NA) crystal were firstly explored through Hirshfeld surface analysis<sup>1-4</sup> with the aid of CrystalExplorer17 package,<sup>5</sup> and 2D fingerprint plot for O $\cdots$ H intermolecular contacts along with energy frameworks for crystal packing were obtained. Then, the HBs were further identified and visualized by QTAIM (quantum theory of atoms in molecules)<sup>6</sup> and RDG (reduced density gradient)<sup>7</sup> methods on the basis of electron density analysis performed with Multiwfn3.6 program.<sup>8,9</sup> Finally, the nature of HB interactions was probed by SAPT (symmetry adapted perturbation theory)<sup>10</sup> calculation with the help of PSI4 code,<sup>11</sup> and the theoretical level of SAPT2+(3) $\delta$ MP2/aug-cc-pVTZ was employed because of high accuracy.<sup>12</sup>

## 2. RESULTS AND DISCUSSION

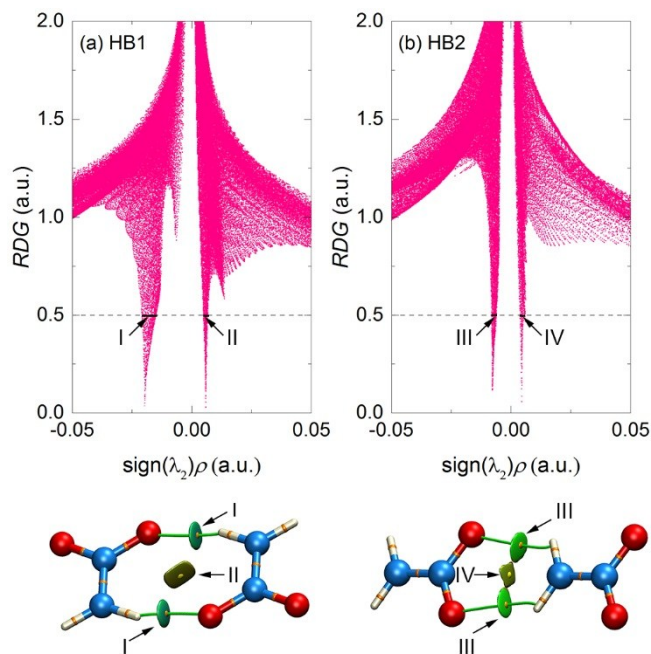
The optimum structure of NA crystal is shown in **Figure S1**, which contains four molecules in the unit cell and belongs to a monoclinic system with the symmetry of C2/c. Layered packing pattern of NA crystal is observed and likes the TATB crystal. In each layer, one NA molecule can form eight intermolecular HBs with the nearest four molecules, leading to a HB network. Two kinds of HB are determined on the basis of geometry criterion and are labeled as HB1 (O $\cdots$ H = 2.00 Å,  $\angle$ N-H $\cdots$ O = 163.91° ) and HB2 (O $\cdots$ H = 2.54 Å,  $\angle$ N-H $\cdots$ O = 120.81°), respectively. The Hirshfeld surface analysis generates a typical fingerprint of HB in **Figure S1c**, and the HB population occupies 67.1% of total intermolecular contacts, suggestive of a HB-rich crystal.

As depicted in **Figure S1d, e, and f**, the energy frameworks manifest that the total interaction energies of NA crystal are mainly derived from the electrostatic contribution that is also the dominant component of HB interactions. Similar to the TATB crystal, the inter-layer interactions are relatively weak, compared with the strong intra-layer HB interactions. Furthermore, it can be found that the strength of HB1 is stronger than HB2, which is consistent with the judgment from the geometrical criterion.



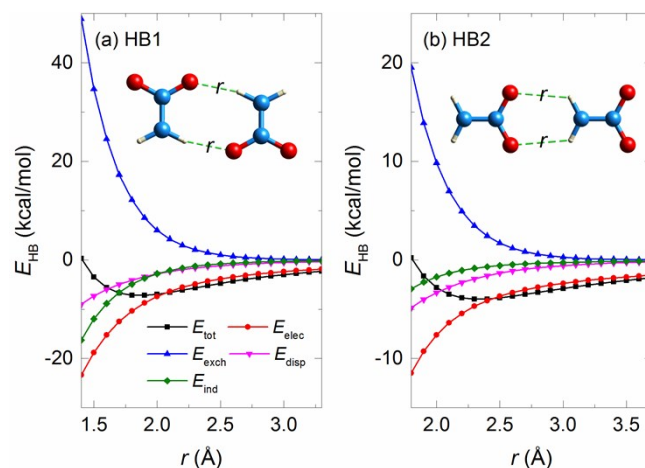
**Figure S1.** (a) Crystal structure of NA along the direction of  $b$  axis. (b) hydrogen-bond pattern in the NA layer. (c) fingerprint plot for  $H\cdots O$  intermolecular contacts in the NA crystal. Energy frameworks for separate electrostatic (d) and dispersion (e) contributions to the total nearest neighbor pairwise interaction energies (f). The cylinders link molecular centroids, and their thickness is proportional to the magnitude of the energy. For clarity, pairwise energies with magnitudes less than 5 kJ/mol are omitted.

To further identify the HBs in the NA crystal, two dimers that are extracted from the crystal structure and only consisted of HB1 and HB2, respectively, were investigated via RDG and QTAIM topography analysis based on the electron density. As delineated in **Figure S2**, there exist bond critical points and bond paths between O atom of the nitro group and H atom of the amino group in the two dimers, demonstrative of the HB formation, which can be visualized by the RDG isosurface. Besides, the steric interaction was confirmed through the RDG profile and ring critical point as a result of the ring structure induced by the intermolecular HBs. The HB strengths were empirically assessed as half of the potential energy density at the bond critical point proposed by Espinosa et al.<sup>13</sup> The strengths of HB1 and HB2 were calculated as -8.41 kcal/mol and -3.00 kcal/mol, which belongs to a weak and moderate HB, respectively, according to the classification suggested by Jeffrey.<sup>14</sup>



**Figure S2.** RDG profile as a function of  $\text{sign}(\lambda_2)\rho$  for (a) HB1 and (b) HB2 dimers and the corresponding isosurfaces of  $\text{RDG}=0.5$  a.u. along with QTAIM topography analysis results.

To delve into the nature of the HB interaction among the NA molecules, the SAPT calculations were performed to decompose the total interaction energy ( $E_{\text{tot}}$ ) into various physical terms, including electrostatic ( $E_{\text{elec}}$ ), exchange ( $E_{\text{exch}}$ ), dispersion ( $E_{\text{disp}}$ ), and induction ( $E_{\text{ind}}$ ) contributions in the course of NA dimer separation. It is obvious from **Figure S3** that the variation trends of SAPT interaction terms are similar for the two dimers. The attractive contributions to the total interaction energy originate from the electrostatic, dispersion, and induction terms, while the exchange component plays a repulsive role. Compared with dispersion and induction contributions, the electrostatic and exchange terms are more sensitive to the separating distance of intermonomer, which are both significantly strengthened with the decrease of HB distance. In keeping with the results obtained from energy frameworks in **Figure S1**, the electrostatic interaction dominates the HB formation and has the most contributions to the overall stability of the complex. Additionally, the interaction energies of HB1 and HB2 are estimated as  $-7.19$  kcal/mol and  $-3.98$  kcal/mol, respectively, from the minimum of the total interaction energy curve.



**Figure S3.** The interaction energy components of hydrogen bond in the NA dimmer of (a) HB1 and (b) HB2 calculated by SAPT as a function of O $\cdots$ H distance.

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