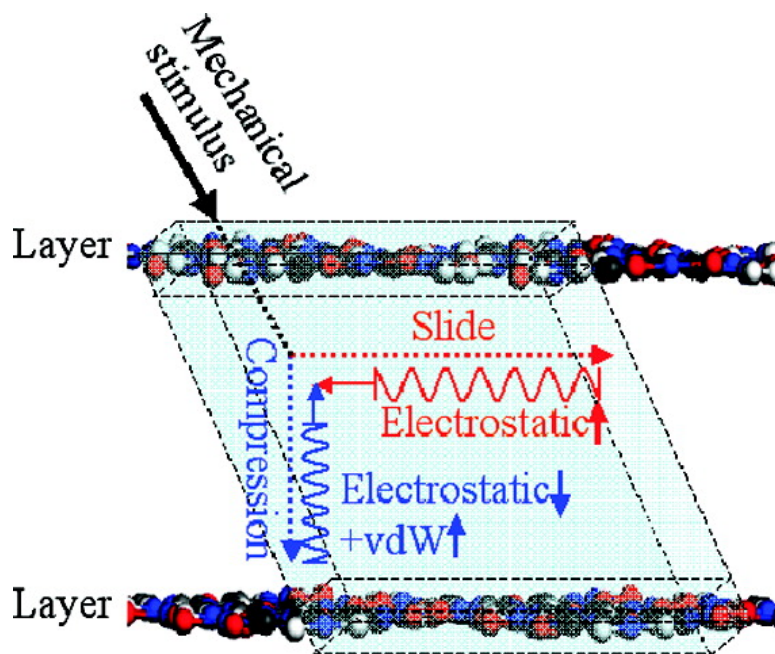


## #-Stacked Interactions in Explosive Crystals: Buffers against External Mechanical Stimuli

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## $\pi$ -Stacked Interactions in Explosive Crystals: Buffers against External Mechanical Stimuli

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**Abstract:** The  $\pi$ -stacked interactions in some explosive crystal packing are discussed. Taking a typical  $\pi$ -stacked explosive 2,4,6-trinitrobenzene-1,3,5-triamine (TATB) as a sample and using molecular simulations, we investigated the nature of the  $\pi$ -stacked interactions versus the external mechanical stimuli causing possible slide and compression of explosives. As a result, between the neighbor layers in the TATB unit cell, the electrostatic attraction decreases with a little decrease of vdW attraction when its top layer slides, whereas the vdW attraction increases with a decrease of electrostatic attraction when TATB crystal is compressed along its *c* axis. Meanwhile, we studied the correlation between the  $\pi$ -stacked structures and the impact sensitivities of explosives by means of three representatives including TATB with typical planar  $\pi$ -stacked structures, 2,2-dinitroethylene-1,1-diamine (Fox-7) with wavelike  $\pi$ -stacked structures, and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) without  $\pi$ -stacked structure. The results showed that  $\pi$ -stacked structures, particularly planar layers, can effectively buffer against external mechanical stimuli. That is,  $\pi$ -stacked structures can partly convert the mechanical energy acting on them into their intermolecular interaction energy, to avoid the increase of the molecular vibration resulting in the explosive decomposition, the formation of hot spots, and the final detonation. This is another reason for the low mechanical sensitivity of  $\pi$ -stacked explosives besides their stable conjugated molecular structures.

### Introduction

Maybe too much attention has been paid to the security and detonation properties of explosives, and some properties attributed to their organic nature are overlooked. For example,  $\pi$ -stacked interactions can also exist in explosive systems and influence their properties. This paper attempts to explain this phenomenon, in particular the nature of the  $\pi$ -stacked interactions against external mechanical stimuli using molecular simulations together with some experimental evidence. As an expansion in  $\pi$ -stacked interaction researches, it may be instructive to understand the sensitivity mechanism of explosives and look for new better energetic materials with appropriate sensitivities. This paper includes four sections: the first shows the  $\pi$ -stacked phenomena in explosives; taking a typical  $\pi$ -stacked explosive TATB as a sample, we explore the nature of the  $\pi$ -stacked interactions in explosives against external mechanical stimuli in the second section. The third mainly indicates that the  $\pi$ -stacked structures in explosives are very helpful to decrease their mechanical sensitivities and to enhance their mechanical stabilities; and finally, some conclusions about the  $\pi$ -stacked interactions in explosives are drawn.

### 1. $\pi$ -Stacked Interactions in Explosive Crystals

Strong attractive interactions among  $\pi$ -systems have been known for a long time. They are involved in many structures and control many phenomena such as the stable double helical DNA,<sup>1</sup> the packing of aromatic and other conjugated molecules in their crystals,<sup>2</sup> some self-assemblies of  $\pi$ -systems,<sup>3</sup> and so forth. To date, adequate attention to these  $\pi$ -stacked interactions

in explosive crystals has not been paid. As a matter of fact, they exist in many explosives and influence explosive properties, especially crystal packing. We find they have an obvious effect on explosive mechanical sensitivities.

The  $\pi$ -stacked interactions in explosives can be indeed confirmed by the planar conjugated molecular structures and the layered crystal packing with reasonable interlayer spacing of three explosives TATB,<sup>4</sup> 3,5-dinitropyrazine-2,6-diamine-1-oxide (LLM-105),<sup>5</sup> and Fox-7<sup>6</sup> illustrated in Figure 1, i.e., 2.8, 3.0, and 3.1 Å for TATB, LLM-105, and Fox-7, respectively, close to that of typical  $\pi$ -stacked porphyrin-porphyrin stacking in its crystal, 3.4 Å.<sup>7</sup> Compared with the typical  $\pi$ -stacked systems such as benzene and graphite, the three explosives have no dissimilarity: TATB possesses planar layered packing like graphite,<sup>8</sup> and LLM-105 and Fox-7 possess wavelike layered

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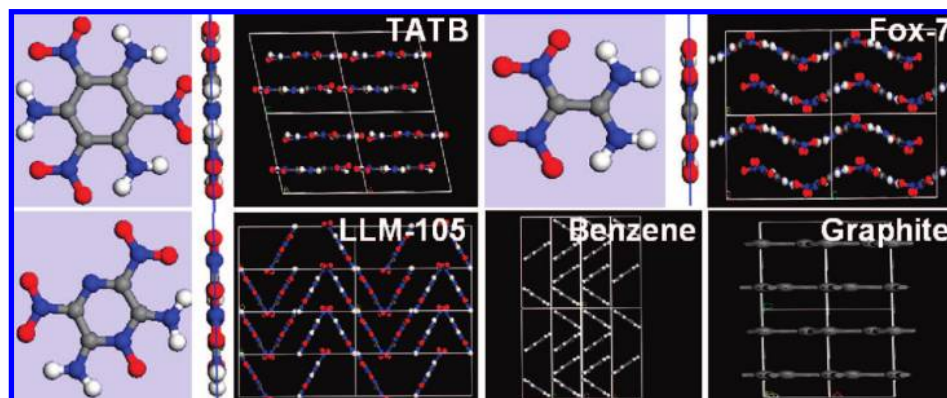
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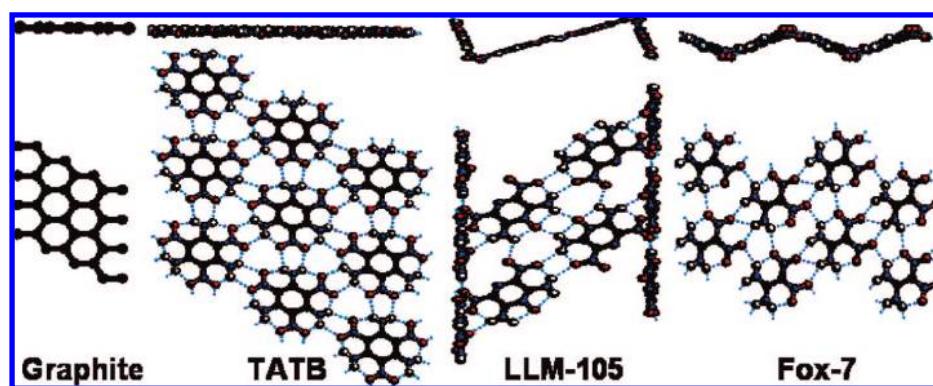
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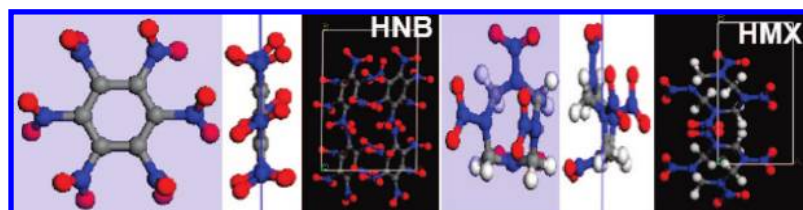
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**Figure 1.** Planar structures of TATB, LLM-105, and Fox-7 molecules in the gas phase and experimental layered structures of benzene, graphite, and three  $\pi$ -stacked explosives illustrated by  $2 \times 2 \times 2$  supercells. C, N, O, and H atoms are indicated in gray, blue, red, and white, respectively.



**Figure 2.** Side (top) and top (bottom) views of the single layer structures in the crystal packing of graphite, TATB, LLM-105 and Fox-7. C, N, O, H atoms, and hydrogen bonds are respectively indicated in gray, blue, red, and white and by green dashed lines.



**Figure 3.** Molecular structures and crystal packing of two explosives HNB and HMX without  $\pi$ -stacked interactions.

packing like benzene in solid state.<sup>9</sup> Figure 2 highlights the hydrogen bonds in the crystal packing of three explosives. Therefore, the nature of the crystal packing of three explosives is attributed to hydrogen-bond-aided  $\pi$ -stacking.

Obviously, conjugated structures and equivalently  $\pi$ -systems are necessary for forming the  $\pi$ -stacked structures in explosives. From above-mentioned crystal packing, we find that the TATB molecules with big  $\pi$ -bonds of 18 atoms and 24  $\pi$  electrons denoted as  $\Pi_{18}^{24}$  form planar layers, and the interlayer interactions are almost all of  $\pi$ -stacked interactions, whereas the LLM-105 molecules with  $\Pi_{15}^{20}$  bonds and the Fox-7 molecules with  $\Pi_{10}^{12}$  bonds form wavelike layers, and the interlayer interactions are partially of  $\pi$ -stacked interactions. Figure 3 indicates no layered structure in hexanitrobenzene (HNB) and HMX<sup>10</sup> due to the big molecules with only the small conjugated structures. Owing to six nitro groups with strong repulsion among them and

noncoplanar with benzene ring, there is no big conjugated structure and further no  $\pi$ -stacked crystal packing in HNB.<sup>11</sup> Similarly, too many nonconjugated atoms in HMX lead to no big conjugated structure and further no  $\pi$ -stacked crystal packing. It therefore seems that a bigger planar  $\pi$ -system with fewer other structures can more readily form layered crystal packing with strong  $\pi$ -stacked attraction. In addition, it can be seen from Figures 1 and 2 that these hydrogen bonds are useful to keep the layered structures, thereby the aid of hydrogen bonds in forming  $\pi$ -stacked structures cannot be negligible.

## 2. Nature of $\pi$ -Stacked Interactions Against External Mechanical Stimuli: A Sample of TATB

It has been experimentally confirmed that the explosives with  $\pi$ -stacked geometries have low mechanical sensitivities and are used as insensitive explosives or desensitizers. One of mechan-

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(11) Here, the molecular structure of HNB is the calculated result using DFT/BLYP/DNP in Dmol<sup>3</sup>, and the crystal structure is from the Polymorph Predictor simulation result due to the lack of experimental.

ical sensitivities, impact sensitivity, is used to show the stability of an explosive versus impact and is measured by the height  $H_{50}$ , from where a given weight falling upon the explosive gives a 50% probability of initiating an explosion. The shorter this drop height, the greater the sensitivity. For example, TATB is the so-called *wood explosive* with almost the lowest impact sensitivity in all explosives, i.e. the highest  $H_{50} = 4.9$  m; whereas those of HNB, 1,3,5-trinitro-1,3,5-triazinane (RDX) and HMX without  $\pi$ -stacked crystal packing are only 0.12, 0.28 and 0.32 m, respectively.<sup>12</sup> At the same time, it was reported that the  $\pi$ -stacked graphite can evidently decrease the mechanical sensitivity, i.e. enhance  $H_{50}$  of mixed explosives.<sup>13</sup> This shows that  $\pi$ -stacked structures can remarkably decrease explosive mechanical sensitivities, acting as buffers against external mechanical stimuli. In spite of many fruitful researches on the correlation between the molecular structures and stabilities of explosives,<sup>14</sup> those on  $\pi$ -stacked interactions in explosive are still overlooked. In this section, we address this issue by means of molecular simulations. As discussed above, the TATB molecules with  $\Pi_{18}^{24}$  bonds and intermolecular hydrogen bonds build the graphite-like crystal packing with big and reciprocally parallel  $\pi$  systems. Namely, the interlayer interactions are typically and basically the  $\pi$ -stacked interactions. Accordingly, this typical  $\pi$ -stacked explosive is taken as an example to explore the nature of the  $\pi$ -stacked interactions and their influences on mechanical sensitivity mechanism. The simulations include following two procedures:

The first is to establish a forcefield for TATB crystal and calculate the  $\pi$ -stacked interactions in it. We found that the general molecular forcefields such as COMPASS<sup>15</sup> and PCFF<sup>16</sup> poorly describe TATB crystal. Therefore a special forcefield was necessary. Previous work has showed the derivated TATB molecular structures from DFT methods are all planar or roughly planar, but those from MP2 are not planar—all the nitro and amino groups deviate 20–30 degrees from the benzene ring.<sup>17</sup> This showed the DFT calculation results are consistent with the planar structures in X-ray diffraction. We accordingly select a DFT method B3LYP/6–311G(d, p) with a periodic boundary condition<sup>18</sup> to relax TATB molecules in the unit cell by constraining the lattice parameters, due to the inaccuracy of the hydrogen atoms' positions brought by the limit of the X-ray diffraction method in ref 4. After optimization, the initial 0.839–1.067 Å lengths of N–H bonds change to the reasonable values within 1.00–1.04 Å, and the central sites of top and bottom TATB molecules in unit cell change slightly. All these prove the method adequate. And the optimized structure is used as the initial one for following calculations.

To discuss the  $\pi$ -stacked interactions in TATB crystal, we keep the  $\pi$ -structured TATB molecules rigid in the crystal and only translate them to somewhere required, then calculate the single point energy for the crystal containing translated structures at B3LYP/6–311G (d, p) level without any variation of lattice parameters. These translations of rigid TATB molecules can meet the requirements of the assumption in building a model for calculating TATB crystal against external mechanical stimuli. Evidently, the energy variation after two  $\pi$ -structures' interactions ( $\Delta E_{\text{inter}}$ ) is the  $\pi$ -stacked interaction energy, which is actually the intermolecular interaction energy ( $E_{\text{total}}$ ) described as van de Waals (vdW) and electrostatic interactions like usually done in dealing with general intermolecular interactions.<sup>7</sup> Here, without respect to the intramolecular interactions, then  $E_{\text{total}}$  can be simplified as eq 1. That is to say, we always keep TATB molecules rigid and only consider the interlayer interactions.

$$E_{\text{total}} = \Delta E_{\text{inter}} = E_{\text{vdW}} + E_{\text{electrostatic}} \quad (1)$$

where

$$E_{\text{vdW}} = \sum_{\text{pairs}(i,j) i < j} \left( \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6} \right) \quad (2)$$

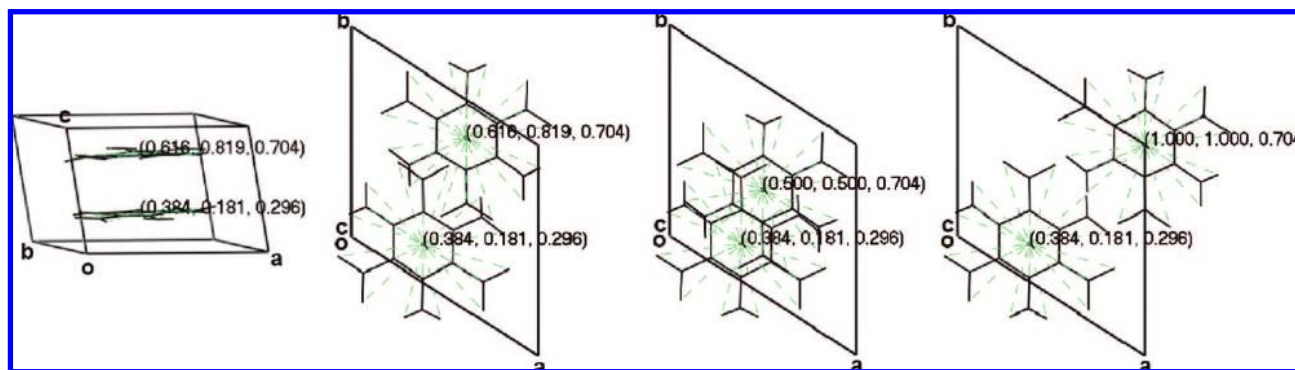
$$E_{\text{electrostatic}} = \sum_{\text{pairs}(i,j) i < j} \frac{q_i q_j}{\epsilon r_{ij}} \quad (3)$$

By holding the atomic electrostatic potentials (ESP) of the TATB molecule optimized from DFT calculation constant, and employing above three equations and Direct Force Field (DFF) program,<sup>19</sup> we establish a molecular forcefield based on DFT calculations for sequential calculations, whose validity is confirmed by the very consistent values derived from the DFT and the force field calculations. By the way, this approach to a particular forcefield based on molecular translations without consideration of intramolecular interactions, i.e., without intramolecular interaction terms, may be instructive to the researches on other  $\pi$ -stacked interactions, which is different from traditional ones always including intramolecular interaction terms.<sup>20</sup>

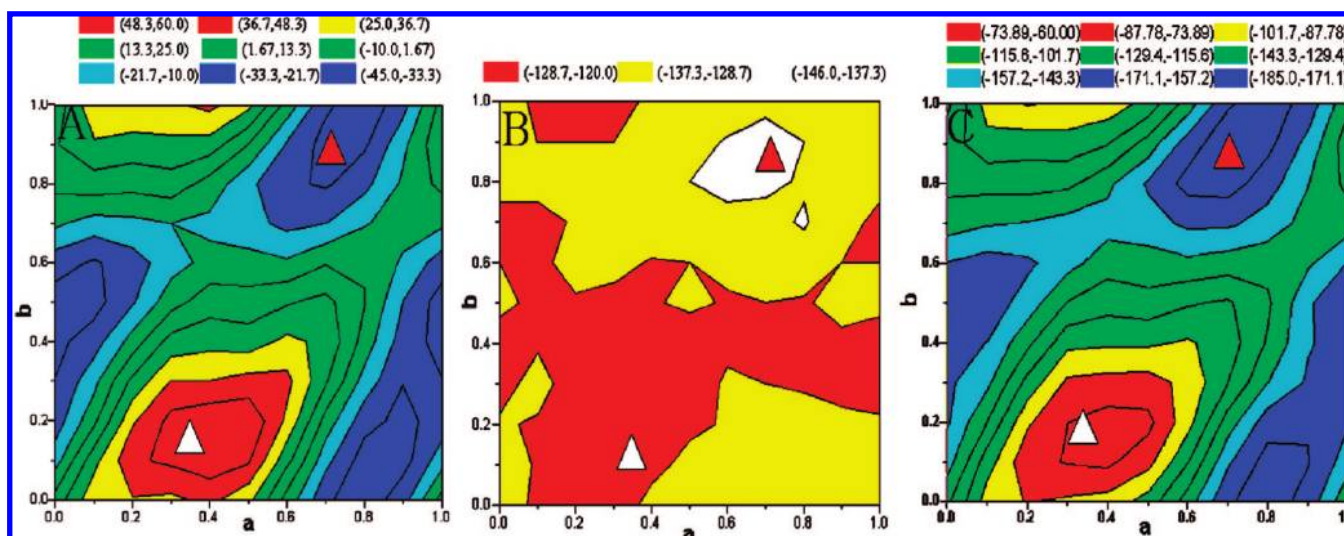
Next, we built a model for calculating TATB crystal against external mechanical stimuli. We hypothesize the external mechanical stimuli acting on TATB crystal can only result in the translations of the  $\pi$ -structured layers like above-mentioned rigid bodies without causing other changes such as the rotation, rupture or deformation of the layers. This case is to a certain extent similar to some mechanical stimuli such as impact, friction and shock waves acting on TATB crystal.<sup>21</sup> Namely, only the slide parallel to the layers and the compression perpendicular to the layers can counteract the mechanical interactions under the slide and compression conditions to investigate the  $\pi$ -stacked interaction changes induced by external mechanical stimuli. For the sliding simulations, only the simplest slide of a single layer in the unit cell is discussed here. Obviously, this slide takes place along the (001) crystal face when keeping the interlayer distance and the molecular orientation invariable. Owing to the periodical conditions and for the convenience of discussion, we keep all the lattice parameters

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**Figure 4.** Scanning and static model for the sliding simulation of TATB crystal. From left to right: a stereo view of relaxed TATB crystal, a view perpendicular to (001) face, and views of the crystal with translating the top molecular center to two points with  $a$ - $b$  fractional coordinates, (0.5, 0.5) and (1.0, 1.0), respectively.



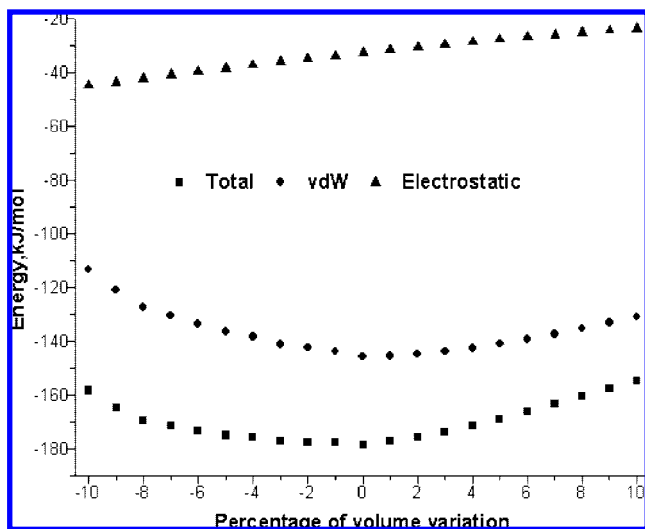
**Figure 5.** Sliding Contour plots of TATB showing the electrostatic (A), vdW (B), and total interaction energy (C) (in kJ/mol) versus the  $a$ - $b$  fractional coordinates of the geometrical center of the top TATB molecule in the unit cell. The red and white triangles correspond to the centers of top and bottom TATB molecules in the unit cell, whose  $a$ - $b$ - $c$  fractional coordinates are (0.616, 0.819, 0.704) and (0.384, 0.181, 0.296), respectively.

and the bottom layer fixed and move only the top layer with a sliding step of  $0.1a$  and  $0.1b$  (Figure 4), and then calculate the energy including vdW and electrostatic contributions of each sliding point, which was the fractional coordinate of the center of the top TATB molecule. It is actually the scanning and static calculation. Linking all energy points together, we can obtain an energy surface illustrated in Figure 5. For compression simulations, because experiments and calculations have showed that the most possible compression and expansion of TATB crystal all occur along its  $c$  axis,<sup>17,21</sup> we calculate the  $\pi$ -stacked interaction energy of TATB crystal under the equal proportional compression similar to an actual shock wave compression along  $c$  axis, in which only the length of  $c$ -axis changes with 1% step, the other lattice parameters and the fractional coordinates of all atoms are fixed.

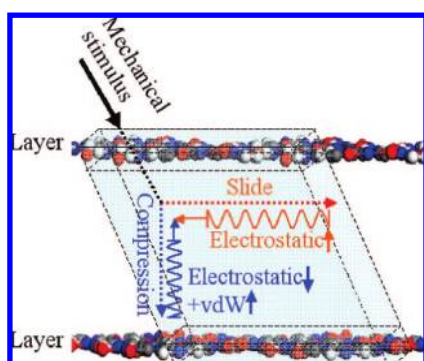
The first result indicated in Figure 5 is of the slide. Four points can be obtained from the figure: (1) the negative interaction energy within  $-60$  to  $-185$  kJ/mol means the total interlayer interactions are always attractive (Figure 5 C); the negative interaction energy within  $-120$  to  $-137$  kJ/mol indicates the vdW interactions are also always attractive (Figure 5 B); whereas the electrostatic interactions can be attractive or repulsive as the interaction energy varies from  $-45$  to  $60$  kJ/mol (Figure 5 A); (2) the vdW interactions have a variation magnitude of only

17 kJ/mol much less than electrostatic interactions with a magnitude of 105 kJ/mol. It implies the latter have greater influences on the total interaction energy. It explains that A and C in Figure 5 are very similar; (3) the electrostatic interaction is the most repulsive when top and bottom centers overlapped, and the most attractive on the initial point corresponding to the optimized structure, very close to the experimental point as mentioned above; (4) sliding from the initial point causes the electrostatic attraction decrease with a little decrease of vdW attraction. This suggests that the electrostatic interaction is important in determining the  $\pi$ -stacked geometry in TATB crystal like porphyrin-porphyrin stacking in its crystal.<sup>7</sup> It shows that mechanical energy leading to the layer slide can be obviously changed into the  $\pi$ -stacked interaction energy, mainly the electrostatic interaction energy between neighbor layers.

The second result is of the equal proportional compression and expansion with 0–10% change rates. From Figure 6 we can find that: (1) the interlayer electrostatic interactions in this case are attractive, and the attraction increases with the compression increasing; (2) the biggest vdW attractive point corresponds to the initial point, and the vdW attraction decreases with increasing of both compression and expansion; (3) that the increasing vdW interaction energy counteracts the decreasing electrostatic interaction energy makes a few change of total



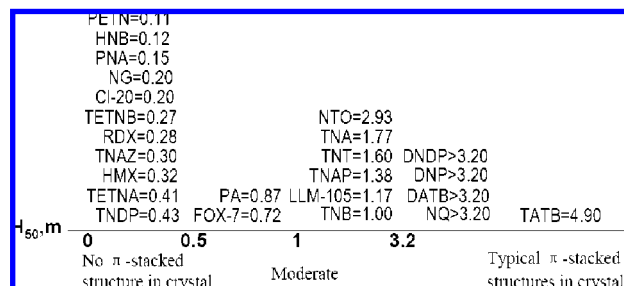
**Figure 6.** Dependences of electrostatic, vdW, and total energy on the rate of equal proportional compression or expansion along  $c$  axis of TATB crystal.



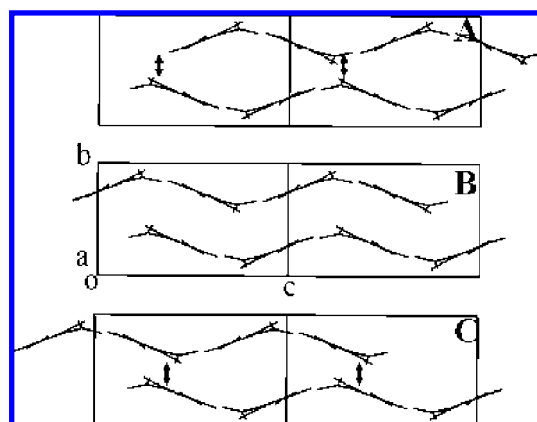
**Figure 7.** Plot showing that  $\pi$ -stacked interactions in TATB crystal buffer against external mechanical stimuli: any mechanical stimulus acting on the crystal can be analyzed into two forces—one force leading to the slide and another leading to the compression of the  $\pi$ -structured layer; to increase the electrostatic energy is to counteract the first force; and to increase the vdW energy and to decrease the electrostatic energy are to counteract the second (all energy are of algebraic values).

energy under the compression to a certain extent close to practice. That is to say, according to  $P = -\Delta E/\Delta V$  at or close to absolute zero where  $P$ ,  $\Delta E$ , and  $\Delta V$  are respectively the internal stress, the energy, and volume variations after compression, little internal stress will take place in TATB crystal under certain compression along  $c$  axis, which is very helpful to buffer external mechanical stimuli and decrease its mechanical sensitivity. This point will continue to be discussed in the next section.

From above discussion on the  $\pi$ -stacked interactions in TATB crystal, we find that the slide of a layer mainly results in the decrease of electrostatic attraction with a little decrease of vdW attraction, but the compression perpendicular to the layer leads to a double effect including the increase of vdW attraction and the decrease of electrostatic attraction. Meanwhile, we define the energy change after sliding from the initial point as sliding barrier  $E_{ab}$ . According to our calculated results using forcefield method here, the biggest  $E_{ab}$ , i.e., the total energy difference of two points respectively corresponding to the red ( $-60$  kJ/mol) and white ( $-171$  kJ/mol) triangles in Figure 5C is 111 kJ/mol,



**Figure 8.** Array of explosives according to their  $H_{50}$  cited from ref 24. Abbreviations: CI-20: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.0.5,9.0.3,11]dodecane; DNP: 2,4-dinitrophenol; DNDP: 4,6-dinitro-1,3-diphenol; NG: nitroglycerin; NQ: nitroguanidine; NTO: 5-nitro-1,2-dihydro-3H-1,2,4-triazol-3-one; PA: picric acid; PETN: pentaerythritol tetranitrate; PNA: pentanitroaniline; TETNA: 2,3,4,6-tetranitroaniline; TETNB: 1,2,3,5-tetranitrobenzene; TNAP: 4-amino-2,3,5-trinitrophenol; TNAZ: 1,3,3-trinitroazetidine; TNB: 1,3,5-trinitrobenzene; TNBP: 2,4,6-trinitro-1,3-diphenol; TNT: 2,4,6-trinitrotoluene; TNTP: 2,4,6-trinitro-1,3,5-triphenol.



**Figure 9.** Plot showing the sliding constraint of the top layer in Fox-7 crystal along the  $b$  axis. B is the initial structure, A and C are the slid structures. Arrows point to the constraint locations.

more than that of our previous DFT calculation 78 kJ/mol,<sup>22</sup> but still much less than its apparent activation energy of thermal decomposition 215 kJ/mol.<sup>23</sup> All these mean that the external mechanical stimuli leading to the slide of TATB crystal can be partly converted into electrostatic potentials without causing TATB molecular decomposition, and the compression of TATB crystal can be efficiently buffered by means of the  $\pi$ -stacked interactions in the crystal with less internal stress. It is the nature illustrated in Figure 7 of  $\pi$ -stacked interactions in TATB crystal against external mechanical stimuli.

### 3. Effect of $\pi$ -Stacked Structures on Explosive Mechanical Sensitivities

To clarify the effect of the  $\pi$ -stacked structures on explosive mechanical sensitivities, we collect 24 explosives with or without a  $\pi$ -stacked structure in their crystal packing in Figure 8. From Figure 8 we can roughly conclude that the explosive with typical  $\pi$ -stacked structures such as TATB possesses very low mechanical sensitivity, whereas those without  $\pi$ -stacked structure such as PETN and HNB possess very high mechanical sensitivities. Conjugated molecular structures forming  $\pi$ -stacked

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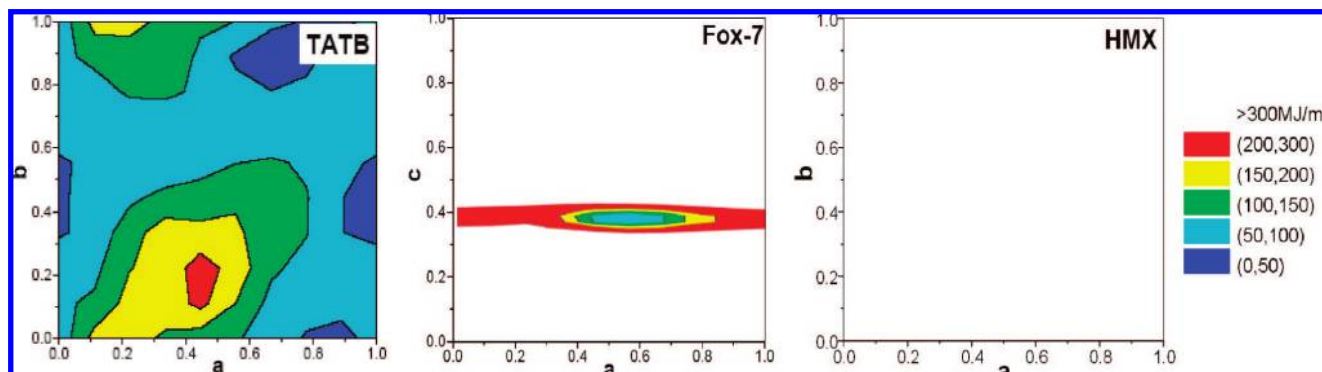


Figure 10. Contour plots showing  $E_{sb}$  of three explosives.

structures are certainly in favor of the stable explosives with low mechanical sensitivities, and they are the reasons for the low sensitivities only on a molecular level.<sup>14</sup> This section discusses the explosive sensitivity from crystal packing, other than from molecular structures only. With respect to the characteristic of the crystal structures in Figures 1, 2 and 3, we select 3 explosives as interested objects including above-discussed TATB with typical  $\pi$ -stacked structures, Fox-7 with  $\pi$ -stacked structures, and HMX without  $\pi$ -stacked structure in crystal packing.

DFT method (BLYP with DNP basis set) in Dmol<sup>325</sup> is performed to complete all calculations on the slide and compression of three explosives. All explosive molecules are at first relaxed with fixed lattice parameters, and then conditionally constrained according to different requirements as done as for TATB crystal in section 2. Namely, for the slide simulations, only the most possible slide parallel to a-c plane and  $\pm 0.1c$  offset along  $c$  axis are considered for Fox-7 due to its wavelike layers in crystal (Figure 9); random calculations are done for HMX and all  $E_{sb}$  results are found to be very high and unreasonable; and the previous data of TATB's slide are cited from ref.<sup>22</sup> Considering the difference between the two kinds of unit cells (i.e., the unit cell volumes of TATB and Fox-7 are 442.49 and 519.32 Å<sup>3</sup>, respectively) and the external mechanical forces acting on the explosive crystals,  $E_{sb}$  is converted from mol units into volume units. That is to say, it is suggested that the volumes of mechanical force acting on different crystals are the same, and then a level to compare  $E_{sb}$  of the previous two crystals is obtained. Additionally, the case of  $E_{sb}$  below 300 MJ/m<sup>3</sup> is discussed here because it is equivalent to 80 kJ/mol<sup>3</sup> for TATB and 93 kJ/mol<sup>3</sup> for Fox-7, far below their apparent activation energies of thermal decomposition.<sup>23</sup> It shows the selected limit for  $E_{sb}$  is reasonable to practice. For the compression simulations, we take into account the 5% uniaxial equal proportional compression with 1% change steps along  $c$  axis for TATB, along  $b$  axis for Fox-7, and along all three axes for HMX. The selections of  $c$  axis for TATB and  $b$  axis for Fox-7 are attributed to their easiest compression orientations.

We can find from Figure 10 that there is a very big difference of sliding behavior among three explosives: TATB and Fox-7 with  $\pi$ -stacked structures can slide, but HMX cannot. It is easy to understand that HMX can not slide due to the strong and

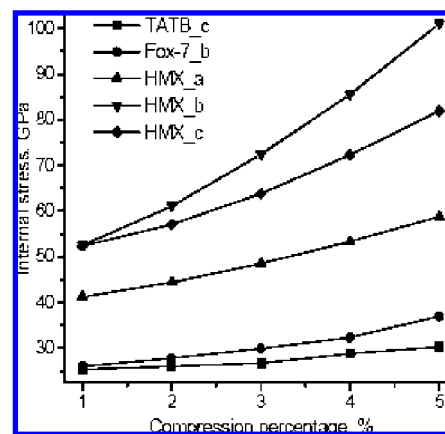


Figure 11. Dependences of internal stress versus uniaxial compression percentage of three explosives.

insufferable intermolecular repulsion and further the thermal decomposition if slid. Owing to the planar layers in TATB crystal packing, interlayer slide can easily occur with a few changes of intermolecular interactions. For Fox-7, the region of  $E_{sb}$  below 300 MJ/m<sup>3</sup> is constrained to a narrow belt, whose offset along  $c$  axis is close to  $0.05c$  and where the most values are above 200 MJ/m<sup>3</sup>. Figure 9 illustrates the obvious constraint of Fox-7's slide. In this case, a little offset can cause a big  $E_{sb}$  due to the rapid increase of intermolecular interactions. Accordingly, TATB can slide freely like graphite, Fox-7 can slide with many constraints, and HMX cannot slide.

It has been confirmed that the formation of hot spot which possibly causes the final detonation has a correlation with the internal stress of explosive.<sup>26</sup> Here, the internal stress of three explosives is approximately calculated using  $P = -\Delta E/\Delta V$ . From Figure 11, we find there is an evident internal stress order for three explosives under the uniaxial equal proportional compression with same compression percentage: TATB (along  $c$  axis) < Fox-7 (along  $b$  axis) < HMX (along  $a$  axis) < HMX (along  $c$  axis) < HMX (along  $b$  axis). This can be well understood—in process of compression, intermolecular interactions change from attraction to repulsion and become stronger and stronger with energy increasing. The increase of the intermolecular repulsion in TATB with typical planar  $\pi$ -stacked structures is the slowest; that in HMX without  $\pi$ -stacked structures is the fastest; and that in Fox-7 with wavelike  $\pi$ -stacked structures is between TATB and HMX.

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In summary,  $\pi$ -stacked structures can indeed influence both slide and compression of explosive caused by external stimuli, similar to the buffers against these stimuli. That is, by converting mechanical energy into intermolecular interaction energy, the  $\pi$ -stacked structures in explosive can partly disperse the mechanical stimuli acting on them to avoid the increase of the molecular vibration leading to the explosive decomposition, the formation of hot spots and the final detonation. It explains why the explosives with  $\pi$ -stacked structures are insensitive versus mechanical stimuli from a viewpoint of crystal. And then, combining the molecular and crystal structures together, we can readily understand the sensitivity rank of explosives in Figure 8. Namely, not only the stable conjugated molecular structures but also the buffering  $\pi$ -stacked crystal structures make the explosives insensitive to mechanical stimuli, such as TATB, DNNDP, DNP, DATB, and so forth; whereas no conjugated molecular structure and no  $\pi$ -stacked crystal structure make the explosives sensitive to mechanical stimuli, such as PETN, HNB, PNA, NG, Cl-20, and so forth.

#### 4. Conclusions

$\pi$ -stacked structures can indeed exist in explosives. Taking a typical  $\pi$ -stacked explosive TATB as a sample, we explore the nature of the  $\pi$ -stacked interactions under the conditions of slide and compression caused by the external mechanical stimuli acting on explosives. For TATB, the slide of crystal layers in

explosive mainly results in the change of electrostatic interactions, and the compression perpendicular to the crystal layers leads to a double effect including the increase of vdW attraction and the decrease of electrostatic attraction. By comparing the slide and compression behaviors of three candidate explosives, TATB with typical planar  $\pi$ -stacked structures, Fox-7 with wavelike  $\pi$ -stacked structures and HMX without  $\pi$ -stacked structures, we find that a  $\pi$ -stacked structure, particularly planar layers in explosive crystal packing, can effectively buffer against external mechanical stimuli. That is, by increasing intermolecular interaction energy,  $\pi$ -stacked structures can partly disperse the mechanical energy acting on them to avoid the increase of the molecular vibration leading to the explosive decomposition, the formation of hot spots, and the final detonation.

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**Supporting Information Available:** The absolute energies and optimized geometries of the calculated structures and the complete citation of ref 18. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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