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Maija M. Kuklja^a; Sergey N. Rashkeev^b

^a Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, USA ^b Center for Advanced Modeling & Simulation, Idaho National Laboratory, Idaho Falls, Idaho, USA

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Molecular Mechanisms of Shear Strain Sensitivity of the Energetic Crystals DADNE and TATB

MAIJA M. KUKLJA¹ and SERGEY
N. RASHKEEV²

¹Department of Materials Science and
Engineering, University of Maryland,
College Park, Maryland, USA

²Center for Advanced Modeling & Simulation, Idaho
National Laboratory, Idaho Falls, Idaho, USA

Simulation of the chemical reactions of decomposition in ideal, defect-containing, and deformed crystalline 1,1-diamino-2,2-dinitroethylene (DADNE) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is performed by means of density functional theory. It is shown that the shear strain deformation plays a crucial role in defining the sensitivity of explosive crystals to initiation and strongly depends on the interactions between the molecules and the crystalline lattice. Based on those calculations, we were able to reveal the important difference in the effects that shear strain has on the chemical properties of these two materials. By focusing on the molecular nature of the shear strain-induced chemistry, we found that the energetic barriers for DADNE decomposition decrease due to shear, whereas those for TATB are not affected by this deformation. This suggests that shear strain may play an important role in defining the sensitivity of hot spots.

Address correspondence to Maija M. Kuklja, National Science Foundation, 4201 Wilson Blvd., Arlington, VA 22230. E-mail: mkukla@nsf.gov

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Introduction

Energetic molecular materials are known for their rapid chemical decomposition, accompanied by a sudden volume expansion and a large energy release. Such materials exhibit the most diverse applications that range from stunning fireworks displays to rocket engine fuels, from national security to railroad construction, and from airbags in automobiles to shock synthesis of new materials. Yet, detailed knowledge of the underlying processes in energetic materials (EMs) is far behind the actual use of energetic materials and device systems. The most desirable features of EMs for practical use are their high performance (a measure of the energy release) and low sensitivity (a measure of the ease of the initiation of chemistry). The lack of fundamental first principles understanding of the chemistry and physics of EMs, coupled with the extraordinary complexity of the initiation of detonation process in EMs, encumbers the design of new energetic systems and the most efficient use of existing materials.

In this study, we perform a comparative first-principles analysis of the initiation of chemistry of a fairly new prospective energetic material, 1,1-diamino-2,2-dinitroethylene (DADNE), and the stability benchmark, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). The perfect structure of a DADNE molecular crystal consists of nearly planar molecules, which are hydrogen-bonded into corrugated sheets, and is described by the P21/n space group with four molecules (56 atoms) per unit cell [1,2] (Figs. 1a, 1c). The unit cell of TATB is triclinic with $\bar{P}1$ symmetry and contains two molecules (48 atoms) [3] (Figs. 1b, 1d). The weak bonding between the layers is largely defined by van der Waals interactions.

This article represents an overview of recently published research on DADNE and TATB in conjunction with the freshly obtained results [4–8]. Features of the solid-state behaviors of the energetic materials are revealed from the physical chemistry

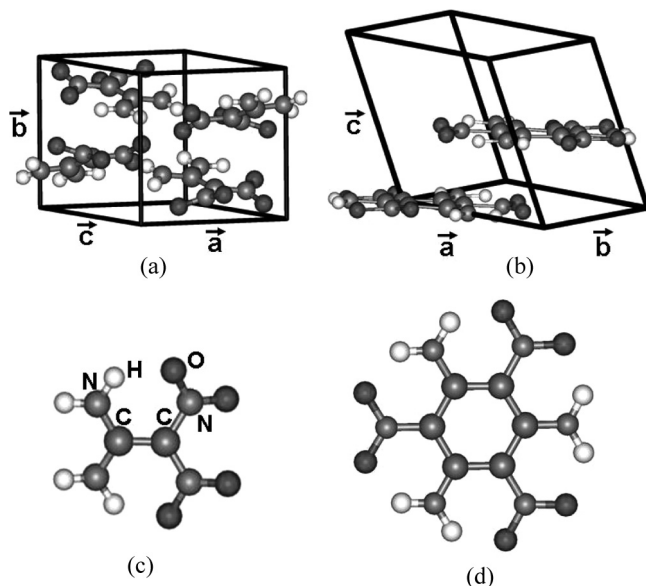


Figure 1. The ideal crystalline (a and b) and molecular (c and d) structures of DADNE and TATB. The C atoms are shown in larger grey balls, O in black balls, N in smaller grey balls, and H in white small balls. The translation vectors of the crystalline structures are also indicated.

point of view. We demonstrate that the decomposition of condensed high explosives is essentially composed of cooperative phenomena, the comprehensive understanding of which requires an integrated approach, a combination of state-of-the-art quantum chemical solid-state calculations, and high-quality experiments. In particular, we focus here on exploring the interplay of early decomposition mechanisms in perfect and imperfect crystals and establish that shear strain-induced deformations are likely to control the initiation of detonation in DADNE and TATB. We also touch upon aspects of autocatalytic reactions and show that an analysis of the crystalline structure, defects, and deformations and the modifications of materials properties induced by them is imperative for understanding

the nature of hot spots and sensitivity to detonation issues in general.

Modeling of Shear Strain Deformation in DADNE and TATB

This work was largely motivated by observations of the anisotropic response of pentaerythritol tetranitrate (PETN) to shock loading [9]. Single PETN crystals shocked normal to the (100) and (101) planes were found to be insensitive, whereas those shocked normal to the (110) and (001) planes were found to be relatively sensitive. Numerical analysis using molecular mechanics indicated that steric hindrance, or the interaction between molecules, was more severe for the (110) and (001) directions, leading to an enhanced energy transfer and greater reactivity [9]. This was verified by additional experiments and semiempirical calculations that implicate a contribution of the shear stress to the sensitivity when the crystal is shocked normal to the (110) planes and thermal initiation when it is shocked normal to the (100) planes [10].

The structure of ideal and deformed DADNE [1,2] and TATB [3] molecular crystals, as well as the crystals containing structural defects, were investigated by means of density functional theory (DFT) calculations within Perdew, Burke, and Ernzerhof's (PBE) [11] generalized-gradient approximation for the exchange correlation, plane waves, periodic supercells, and ultrasoft pseudopotentials for C, N, O, and H atoms, using Vienna Ab-initio Simulation Package (VASP) codes [12].

In order to simulate shear strain deformations in the crystals, we constructed supercells formed by six molecular-layer slabs, separated by a 10 Å layer of vacuum [4,7]. The shear strain was introduced by shifting the three upper layers of the slab relative to the three lower layers in the directions parallel to the crystalline slip plane. An arbitrary shift vector in the **ac**- plane in DADNE is $\mathbf{d} = \gamma_a \mathbf{a} + \gamma_c \mathbf{c}$ (Fig. 2a); for TATB, a similar formula is written for the **ab**- plane: $\mathbf{d} = \gamma_a \mathbf{a} + \gamma_b \mathbf{b}$ (Fig. 2b). The activation barriers for the decomposition and structural rearrangements of the molecules placed at the

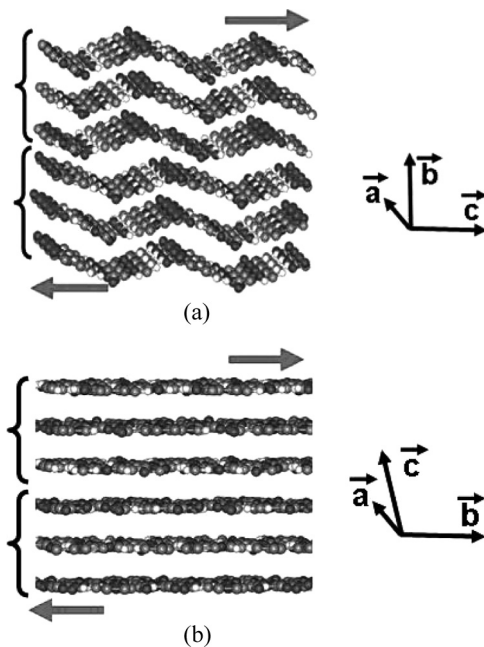


Figure 2. Relaxed six-layer (3 + 3)-slab (in the slab model) of the DADNE (a) and TATB (b) molecular crystals. Bold grey arrows schematically show the directions of the applied shear strain deformation in which the three upper layers are shifted relative to the three lower layers.

interfacial layers (where the shear strain reaches its maximum) were calculated using the nudged elastic band approach [13] for each Δ .

Autocatalytic Aspects of Early Decomposition in Ideal and Deformed DADNE and TATB

Autocatalytic mechanisms—that is, the processes in which intermediate products of the chemical decomposition become catalysts themselves and accelerate further decomposition of the material—are among the least understood and the least studied aspects of initiation [14]. Although it looks obvious that autocatalysis may significantly contribute to the initiation of

detonation, investigations of these phenomena represent extraordinary challenges both experimentally and theoretically, and studies of autocatalytic aspects of initiation are largely lacking [14].

We focus mainly on the dissociation of the C-NO₂ bond because this is a common decomposition reaction in both DADNE and TATB. Besides, it was suggested that the C-NO₂ bond rupture is most affected by the deformation [8] due to the strong interactions between the split-off NO₂ molecule and the crystalline lattice. Conversely, isomerization reactions (HONO and/or CONO) are of intramolecular character [6,8]. The presence of interstitial NO₂ groups affects DADNE and TATB in different ways. In DADNE, the C-NO₂ dissociation barrier of interfacial molecules varies between 93 kcal/mol (for $\gamma_c=0$ and 1) and 43 kcal/mol (for $\gamma_c=0.45$, Fig. 3; the dissociation barrier is much less sensitive to an **a**- shift) [8].

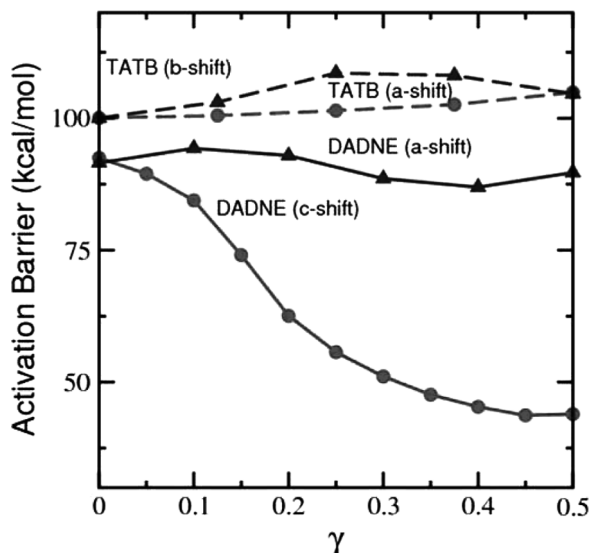


Figure 3. Activation barriers for C-NO₂ homolysis in DADNE (solid lines) and TATB (dashed lines) as a function of shift vectors γ for various shifts (**c** and **a** for DADNE and **a** and **b** for TATB).

To reveal autocatalytic trends (or lack thereof), we probe several consequent dissociation acts that result in the cumulative appearance of NO_2 groups in the interstitial space between molecular layers in the crystalline structures of TATB and DADNE. We observe that the NO_2 group, trapped in the interstitial, tends to increase the shear strain between the layers. For example, at the shear $\gamma_c = 0.1$, the crystalline DADNE slab with one split-off interstitial NO_2 group relaxes to a configuration similar to that with $\gamma_c \sim 0.2$. This increased shear strain lowers the decomposition barrier for breaking the next interfacial C- NO_2 bonds; that is, facilitates further NO_2 decomposition at the interface. In other words, the shear strain reduces the activation barrier of the C- NO_2 rupture, which accelerates the decomposition reactions. An appearance of an NO_2 molecule in the confinement of the interface, in turn, increases the shear level. As the process recurs, its effect is reinforced and, hence, is autocatalytic.

In a perfect TATB crystal, parallel flat graphite-like layers can slide nearly freely; that is, the structure does not produce or accumulate any shear strain (Fig. 2b). An interstitial NO_2 group, trapped between two TATB layers, tends to force the nearest molecules away from each other; it disturbs the planar structure of the interfacial layers by tilting the TATB molecules out of the plane. Such a molecular orientation disorder at the interface increases with an increase in the concentration of interstitial NO_2 molecules. Undoubtedly, this disorder will affect chemistry. However, the number of detached NO_2 groups confined between molecular layers in TATB is greater than in DADNE. A simple estimate shows that the critical number of free interstitial NO_2 groups is about four times higher in TATB than in DADNE. The high concentration of confined NO_2 groups in the TATB structure will cause the molecules to be significantly disoriented and the structure of the layer will be far from the initial planar structure.

Further, interactions between the interstitial NO_2 groups yield primary products, isomers of N_2O_4 , and secondary products, N_2O_x and NO_y . The corresponding reaction energies between interstitial NO_2 molecules are slightly different in the

two materials. The formation of nitrogen oxides with larger molecules (N_2O_4) is more exothermic in the DADNE structure. The secondary formation of oxides (N_2O_5 or NO_3 and NO) is more exothermic in TATB. Although the transformation reactions of nitrogen oxides are only slightly exothermic, they demonstrate that the exothermic chemistry in DADNE and TATB crystals may be triggered early on by the products of very initial endothermic reactions due to the autocatalytic effect. In addition, these results help provide a consistent interpretation to experiments. In particular, although gaseous nitrogen oxide molecules (NO_x and N_2O_y) are always observed in decomposition experiments of nitro compounds, NO_2 is found in much lower concentrations than would be expected due to the splitting off of nitro groups as a primary decomposition reaction [14]. The conclusions obtained here may explain this seeming contradiction by the autocatalytic character of the condensed-phase decomposition.

Relation to Hot Spots

The quality of energetic materials is defined by their low sensitivity to initiation of detonation and high performance. The mechanisms governing performance are fairly well understood, whereas the mechanisms of sensitivity are poorly known and currently extensively studied. Among the least understood are the low-velocity impact ignition mechanisms, in which an energetic solid is subjected to a mild dynamic mechanical loading; they are likely to occur in a variety of accident scenarios. Because the key to initiation of chemistry is proposed to be the formation of localized hot spots [15], factors that influence the dissipation and localization of the mechanical energy and its transfer into thermal energy are strong functions of the material properties. It is widely accepted, for example, that the sensitivity to ignition correlates with the thermal decomposition energy [14]. Relative roles of void collapse, friction, shear, dislocation pile-up, and other postulated hot spot formation mechanisms need to be better determined by both experiments and theory.

An examination of a crystalline arrangement of TATB, in comparison with DADNE, demonstrates that no specific in-plane slips are allowed in the **ab**- plane of TATB. Such rigidity is determined by the high symmetry of the TATB molecule, which results in strong inter- and intramolecular hydrogen bonds in the **ab**- plane. The shear between these layers, however, is not energetically costly because the interlayer overlapping is minimal. This slip does not cause any effects on the dissociation of TATB molecules (and barely affects the electronic structure).

DADNE, on the other hand, lacks molecular symmetry and is built out of polar molecules linked with each other by the cohesion of NO_2 and NH_2 groups located at adjacent molecules. This also creates strong hydrogen bonding in corrugated chains of molecules along the **c**-axis but not in all directions (this is why the shear strain along the **a**-direction produces not so much structural damage). Besides, unlike TATB, several possible motions of DADNE molecules are allowed by symmetry. This results in the appearance of polar surfaces in the structure and allows a richer variety of local structural defects to occur; for example, different conformers [16] or a “flipped” molecule [4]. A major consequence of this defect-induced disorder is attributed to the decomposition barrier decrease and, in turn, the higher sensitivity of DADNE to initiation compared to TATB.

We will now analyze an assumption that the formation of hot spots is totally attributed to the shear strain due to the mechanical loading of the material. Several important observations based on our first-principles calculations would immediately follow from this proposition. We found that the shear strain results in the reduction of the decomposition barrier [6,8] and the reduction of the band gap in DADNE [7]; these are both dynamic effects, which are crucial within a short time after the shear strain was generated by, for example, an impact or a shock wave [7]. We conclude that the reduced NO_2 detachment energy barrier facilitates the decomposition of the interfacial DADNE molecules before the system relaxes [17]. In addition, the band gap reduction of DADNE can trigger sensitivity to

optical and/or thermal stimuli via electronic excitations [18], which can lead to either direct bond breaking or a high population of vibronically hot states [19]. The mechanical relaxation of the system will cause local heating of the material in the vicinity of the deformation; this can be associated with the temperature rise in the hot spots.

After the relaxation has occurred, the decomposition barrier regains its original value as in an ideal crystal, and the decomposition rate may decrease. If the chemical reaction did not spread around far enough by this moment, the initiation will die out. If the chemical reaction propagates to involve other hot spots, the process most likely will be transferred into a chain reaction due to multiplication of excitations, eventually leading to an explosion.

A comparison between TATB and DADNE illustrates that hot spots are likely more complex than just regions with a high density of shear strain-induced defects or deformations. However, if shear strain is taken into account alone, DADNE is predicted to be more sensitive to mechanical loading than TATB, contrary to earlier predictions.

Conclusions

This study only gives us a glimpse into the possible molecular mechanisms of shear strain sensitivity of molecular energetic materials in the course of detonation initiation. We limited our consideration to a single decomposition mechanism, the C-NO₂ bond dissociation in DADNE and TATB. We aimed at illustrating how the interplay among mechanical and chemical processes in energetic molecular crystals may be correlated with their sensitivity and with relevant details of the initiation processes. We showed that the initial products of the chemical reactions interact with the host molecular crystal and may enhance the shear strain (DADNE) or introduce an orientation disorder in the interfacial crystalline layers (TATB). The mechanism(s) of mechanochemical autocatalysis are material dependent and likely to be manifested in significant variations in the behavior of energetic crystals. Though the C-NO₂ decomposition reactions

are endothermic, the subsequent C-NO₂ dissociations in the interlayer confinement require progressively less energy. Exothermic reactions, which are triggered by the interactions of detached interstitial NO₂ groups, start early on in both DADNE and TATB; however, one needs to pump up a greater energy into TATB (and accumulate a higher concentration of interstitial NO₂ groups) before the exothermal chemistry is ignited. Further detailed investigation is needed to reveal all of the complexity of the autocatalytic aspects of the sensitivity to initiation of energetic materials.

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