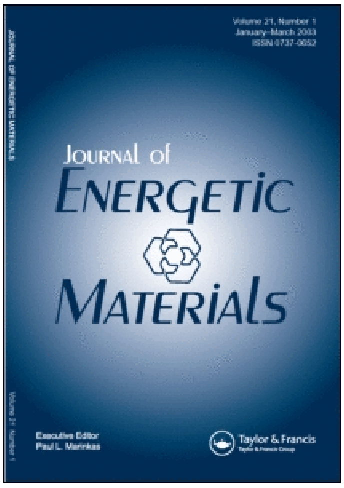

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The Structure and Decomposition Chemistry of Isomer Defects in a Crystalline DADNE

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We simulated substitutional stereoisomer defects in a crystalline 1,1-diamino-2,2-dinitroethylene (DADNE) and studied their atomic and electronic structure and decomposition chemistry. We found that molecular gas phase trans- and cis-isomers are 4.6–6.9 kcal/mol (0.2–0.3 eV) and 11.5–16.1 kcal/mol (0.5–0.7 eV) less stable than DADNE, respectively, which agrees well with earlier studies. We also established that the substitutional trans-isomer defect in the ideal DADNE crystal significantly affects the thermal stability and chemical and physical properties of the solid DADNE matrix, which may imply the existence of alternative synthesis routes for new materials and gives new insight into initiation of detonation in energetic materials.

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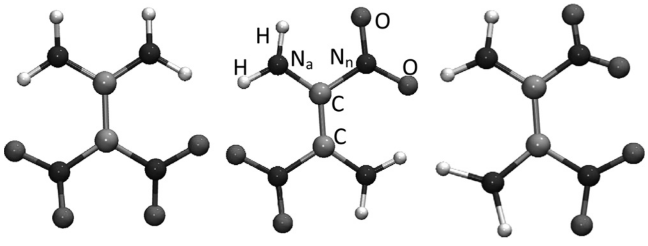
Keywords: *DADNE*, defects, energetic materials, explosive decomposition, isomerization, organic molecular crystals, thermal chemistry

Introduction

During this decade, a molecular crystal 1,1-diamino-2,2-dinitroethylene (DADNE, $C_2H_4N_4O_4$; (also called FOX-7)) [1] has attracted a lot of attention because of its predicted potential applications as a superior energetic material with low sensitivity and high performance [2]. It has functional groups found in common nitramine explosives, such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) [3], and nitroarenes, such as 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) [2]. The relative ease with which it can be synthesized in a basically single-step process, prompted a proposition that DADNE can be used as a building block for design of novel energetic materials [4–6]. Although the structure of DADNE [7] molecule allows for *cis*- and *trans*-isomers to appear [3] (Fig. 1), no DADNE isomers have as yet been synthesized, despite various attempts [6]. In this work, we focus on understanding the interactions in the crystalline ideal and defective DADNE lattice. In particular, stereoisomers of DADNE molecules are considered as simple prototype structural defects, which simulate both regular and perturbed



(a) (b) (c)

Figure 1. Three DADNE isomers: (a) the equilibrium structure, (b) the *trans*-isomer, and (c) the *cis*-isomer, N_a and N_n indicate nitrogen atoms of amino- and nitro-groups, respectively.

molecular interactions in the lattice. In addition to exploring their basic properties, we investigate correlations between the presence of such local defects in the DADNE crystal, the mechanisms of the detonation initiation in solid state, and the stability of the material.

Method

Molecular and solid-state calculations of DADNE were performed by employing computational quantum mechanical and hybrid techniques. In molecular calculations, we used density functional theory and the hybrid B3LYP density functional [8,9] and the coupled cluster theory with double (CCD) and single and double (CCSD) excitations. The electronic structure of the DADNE molecule and its isomers were calculated using the GAUSSIAN 03 code [10] with 6–31 + G(p, d) and correlation corrected double- and triple-zeta basis sets (aug)-cc-pVDZ and cc-pVTZ.

In calculations of the atomic and electronic structure of a DADNE crystal containing a stereoisomer, we employed the embedded cluster method (ECM) as implemented in the GUESS computer code [11–13] with the hybrid B3LYP density functional and 6–21G basis set. The ECM belongs to a broader class of hybrid quantum mechanics/molecular mechanics (QM/MM) techniques in which a small region, considered quantum mechanically and is referred to as QM cluster, is embedded into a classically treated environment. The interaction of the electrons and nuclei inside the QM cluster with the rest of the host lattice; the perturbation of the lattice by the defect, for example, isomer molecule; and the reciprocal effect of the lattice distortion on the defect itself are treated self-consistently. The ECM method with applications to DADNE crystal is detailed elsewhere [13,14]. In this work, we have used a 14-molecule quantum cluster to describe the *trans*-isomer in the crystalline environment. The arrangements of molecules in the QM cluster have been chosen in order to provide a zero dipole moment of the system and full quantum mechanical surrounding of the molecule in the center of the cluster. The energy balances of chemical reactions were calculated as differences between the corresponding total energies of the initial and final states of the system. Transition state configurations were first calculated using the periodic model, Perdew-Burke-Ernzerhof (PBE) density functional [15], and the nudged elastic band method [16] implemented in the VASP code [17] and then refined using the ECM method.

Structure and Properties of DADNE Isomers

Gas-Phase DADNE Stereoisomers

We started this study with simulation of the stereoisomers of DADNE molecules (Fig. 1) in the gas phase. The total energies of the *trans*- and *cis*-isomers calculated using the B3LYP functional and $6\text{–}31+\mathrm{G}(p,d)$ basis set are only 4.6–5.5 kcal/mol (0.20–0.24 eV) and 16.1–16.8 kcal/mol (0.70–0.73 eV), depending on the basis set, higher than the total energy of the ground-state DADNE molecule, respectively. This is in good agreement with earlier work reporting slightly different values of 4.6 kcal/mol (0.2 eV) for the *trans*-DADNE and 18.4 kcal/mol (0.8 eV) for the *cis*-DADNE [3]. We also performed CCD and CCSD calculations of the isomers and found that the total energies of the *trans*- and *cis*-isomers are 5.8–6.7 kcal/mol (0.25–0.29 eV) and 9.9–11.1 kcal/mol (0.43–0.48 eV) higher than that of the DADNE molecule. The geometry configurations obtained by the two methods agree well. These formation energies suggest that we can focus our further work on the *trans*-isomer alone.

The electronic structure of the *trans*-DADNE isomer considerably differs from the electronic structure of the DADNE molecule. The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the *trans*-DADNE is equal to 57.6 kcal/mol (2.5 eV), which is significantly lower than the HOMO-LUMO gap in the ideal molecule (103.8 kcal/mol [4.8 eV]). In the *trans*-DADNE, the HOMO is dominated by the contributions due to orbitals of carbon atoms and nitrogen atoms of amino groups, and it is split up from the second highest occupied electronic level by 30 kcal/mol (1.3 eV). The LUMO is mainly formed by the orbitals of nitro groups. The second lowest unoccupied level, LUMO + 1, which is formed by the molecular orbitals of nitro groups with a partial contribution from carbon atoms, is split up from the LUMO by 50.7 kcal/mol (2.2 eV).

Solid-State Phase Geometry and Electronic Structure of Isomer Defects

Our solid-state ECM calculations show that the defect formation energy of the model crystal containing a single *trans*-isomer molecule is equal to 34.6 kcal/mol (1.50 eV), thus indicating strong interactions of the molecular defect with the lattice. As expected, the molecular structure of the *trans*-isomer in the crystalline environment considerably differs from its structure in the gas phase due to interactions with neighboring molecules. For example, the torsion angles $\angle N_n\text{-C-C-}N_a = 8$ degrees compared to -3 degrees in an isolated molecule [18]. Also, the C=C bond is stretched to 1.41 Å vs. 1.39 Å for a gas-phase isomer molecule yet remains much shorter than the C=C bond in the ideal DADNE molecule (1.47 Å). The presence of the local defect in a crystalline lattice induces the atomic relaxation and hence causes the modification of the electronic structure of the system. The HOMO-LUMO gap of DADNE crystal containing a *trans*-isomer defect is reduced from 80.7 kcal/mol (3.5 eV) for the ideal crystal to 50.7 kcal/mol (2.2 eV) for a crystal with a defect. This is due to a split of HOMO from the top of the valence band (VB). Meanwhile, the position of the conduction band (CB) remains the same with respect to the perfect crystal. The HOMO and LUMO orbitals of the crystal containing an isomer defect have the same nature as those of a single *trans*-isomer molecule.

Stereochemistry

We compare the mechanisms of the decomposition chemistry in a crystalline DADNE, which initiate on a defect *trans*-isomer molecule and on a regular DADNE molecule.

C-NO_2 Bond Homolysis

We simulated the C-NO_2 bond fission reactions, starting from the nitro group in its regular and irregular environments (Fig. 2). For the regular environment, we found that the reaction energy for breaking the C-NO_2 bond is 41.5 kcal/mol (1.8 eV) and the activation barrier is 91.8 kcal/mol (3.98 eV), consistent with the decomposition of an ideal DADNE crystal obtained in periodic calculations [19,20]. Detaching NO_2 species in the irregular environment is hampered by the close location of neighboring nitro groups as their oxygen ions, which are negatively charged, repel the oxygen ions of the detached NO_2 fragment.

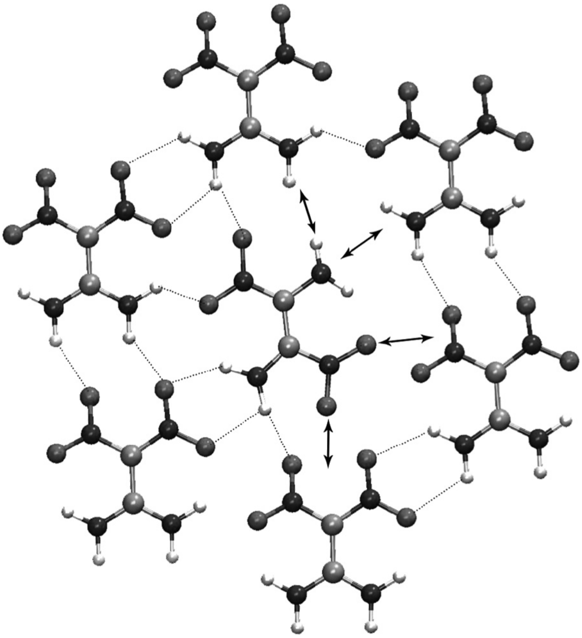


Figure 2. The *trans*-isomer defect in the DADNE lattice. Dotted lines show hydrogen bonding typical for attractive interactions of the *trans*-isomer defect with the lattice (regular environment); arrows indicate repulsive interactions of the *trans*-isomer defect with the lattice (irregular environment).

The reaction energy is equal to 64.6 kcal/mol (2.8 eV) and the activation barrier for detaching the irregularly surrounded NO_2 is 133.7 kcal/mol (5.8 eV), which is significantly higher than the activation energy in an ideal crystal, 94.5 kcal/mol (4.1 eV) [19,20], and by far higher than the experimentally estimated activation energy for the overall decomposition of DADNE, 58 kcal/mol (2.51 eV) [2]. Therefore, we suggest that the substitutional *trans*-isomer would make the C-NO_2 bond fission channel of decomposition unfavorable.

CONO Isomerization and NO Release

Modeling of the C-$NO_2 \rightarrow$ CONO isomerization of the *trans*-DADNE isomer suggests that this reaction is exothermal, leading to the detachment of the NO species in a two-stage process (Fig. 3). A rotation of NO_2 group by 78 degrees requires

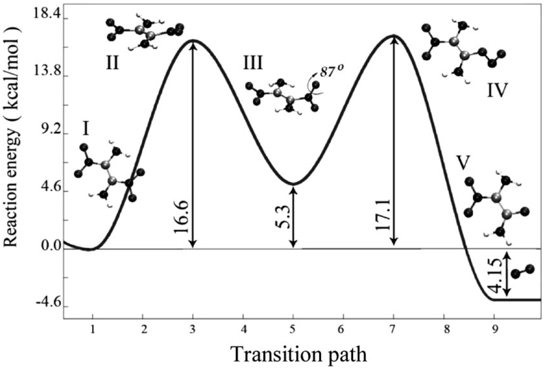


Figure 3. Schematic of the nitro-to-nitrite isomerization followed by CO-NO homolysis is illustrated as a five-step process: (1) the ground state of a *trans*-isomer in a DADNE crystal, (2) the transition state corresponds to a rotation of the nitro group by 78 degrees around the C–NO_2 bond, (3) the relaxed state with rotated NO_2 group, (4) the transition state corresponds to the formation of an unstable CONO *trans*-isomer, and (5) the final state corresponds to detached nitro group with the gain of energy.

16.6 kcal/mol (0.72 eV) to reach the transition state II, and the system gains 11.3 kcal/mol (0.49 eV) in the course of the relaxation to the local minimum III, in which the NO_2 group is rotated by 87 degrees with respect to the ground state configuration I. The further N-O interchange and the consequent detachment of NO species proceed with a barrier of 11.8 kcal/mol (0.51 eV). This process is slightly exothermic, with a reaction energy of 4.2 kcal/mol (0.18 eV). The detached NO species relaxes into the interlayer space and takes the orientation perpendicular to the molecular layer at a distance of 1.75 Å from a host oxygen. The CONO isomerization in an ideal DADNE crystal is endothermic and the corresponding activation energy is 42 kcal/mol (1.82 eV) [19,20], signifying the most favorable decomposition reaction in the ideal crystal. The decomposition via this pathway in the DADNE containing the *trans*-isomer also has a low activation energy and possibly can be triggered by a resonance (or fluctuations) of the rotational frequencies of NO_2 groups. Therefore, this mechanism can be facilitated in the defective material. One may attempt to link this observation to difficulties in synthesis of isomer DADNE materials [6]. It appears that a small perturbation (e.g., due to moderate heat or low-rate shear stress) may resonate with rotational degrees of freedom due to the interactions between neighboring molecules in the vicinity of the *trans*-DADNE molecule. This in turn may trigger decomposition, which requires 16.6 kcal/mol (0.72 eV; see Fig. 3), and may lead to a low or no yield of crystalline *trans*-DADNE. This also implies that isomer DADNE crystals could be crystallized only at low temperatures (if at all).

HONO Isomerization and HONO Release

Our calculations show that the reaction energy for the hydrogen bond switching due to the *intramolecular* hydrogen transfer in *trans*-DADNE is 26.5 kcal/mol (1.15 eV); that is, considerably smaller than that (45.4 kcal/mol [1.97 eV]) found for H transfer in the perfect crystal. The activation energy is 81.9 kcal/mol (3.55 eV), which is 10.4 kcal/mol (0.45 eV) lower than that for the ideal crystal and yet too high to be considered as a primary initiation process under moderate thermolysis conditions.

The results of our calculations of *intermolecular* hydrogen transfer between a *trans*-isomer molecule and the nearest molecules demonstrate that this process does not occur due to strong electrostatic interactions between the proton and the host nitrogen of the amino group (Fig. 2). We therefore suggest that HONO formation can hardly be considered as a precursor for the overall decomposition of solid ideal or defective DADNE under moderate heating conditions.

Conclusions

We have modeled the atomic and electronic structure and the initial decomposition chemical reactions in the condensed phase of a DADNE crystal containing a point structural defect, *trans*-isomer molecule. The obtained results suggest that the presence of such imperfections strongly changes the profile of the adiabatic potential energy surface of the system, thus changing the decomposition chemistry. Indeed, the strong electrostatic repulsion between nitro groups of the *trans*-isomer and the surrounding molecules hampers C-NO_2 homolysis, affects H transfer, and makes CONO isomerization the most favorable exothermic initiation reaction. We therefore suggest that, depending on the quality of samples, decomposition initiates with different reactions. In particular, in ideal crystals, CONO isomerization has the lowest activation energy; in crystals with high concentration of dislocations or grain boundaries, C-NO_2 homolysis is the dominating mechanism [20]; point defects (such as the *trans*-isomer) favor CONO isomerization; and HONO precursors may be formed only when a large amount of energy is available or at later stages of decomposition when exothermic reactions provide the internal energy to self-support the overall decomposition [14].

The scenarios described in this article are based partly on the available theoretical and experimental results and partly on the extrapolation of these results. The apparent lack of a careful characterization of DADNE samples (both polycrystals and single crystals) in the experimental papers leaves some ambiguity in analyzing measurements. Therefore, the models presented here should be considered only as possible coherent interpretations of the results rather than a complete theory.

Acknowledgments

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under high temperature, which would weaken the C=C bond and induce rotations of functional groups around this bond. The structure of 1,2-diamino-1,2-dinitroethylene would theoretically allow for two geometric isomers, *trans*- and *cis*-, to exist.

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