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Solvent effect on the crystal morphology of 2,6-diamino-3,5-dinitropyridine-1-oxide: A molecular dynamics simulation study

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ABSTRACT

The attachment energy (AE) calculations were performed to predict the growth morphology of 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) in vacuum. The molecular dynamics (MD) method was applied to simulate the interaction of trifluoroacetic acid solvent with the habit faces and the corrected AE model was adopted to predict the growth habit of ANPyO in the solvent. The results indicate that the growth morphology of ANPyO in vacuum is dominated by (1 1 0), (1 0 0), (1 0 −1) and (1 1 −2) faces. The corrected AE energies change in the order of (1 1 0) > (1 0 −1) > (1 1 −2) > (1 0 0), which causes the crystal morphology to become very close to a flake in trifluoroacetic acid solvent and accords well with the results obtained from experiments. The radial distribution function analysis shows that the solvent molecules adsorb on the ANPyO faces mainly via the solvent–crystal face interactions of hydrogen bonds, Coulomb and Van der Waals forces. In addition to the above results, the analysis of diffusion coefficient of trifluoroacetic acid molecules on the crystal growth faces shows that the growth habit is also affected by the diffusion capacity of trifluoroacetic acid molecules. These suggestions may be useful for the formulation design of ANPyO.

1. Introduction

Explosives are widely used for both military and civilian applications. In order to reduce the unexpected accidents due to environmental stimuli, such as rough handling, fragment impact and thermal cook-off, there is strong requirement for explosives having both good thermal stability impact and shock insensitivity and better explosive performance in modern ordnance. The sensitivities of explosive versus external stimuli are affected greatly by crystal morphology including crystal shape and size. The growth habit of explosive is determined by both the internal structure factors and the external conditions. A great number of researches have been carried out experimentally and theoretically, and solvent has been found to be one of the most important external factors determining the morphology [1–3].

Experimental approaches and computational simulations are the main methods which are used to research the crystal morphology. However, the former are expensive and time consuming, and, especially, the experimental results cannot provide enough microscopic details about how the solvents interact with the explosive crystal. In contrast, computational models can be used to obtain more detailed insights into the effect of solvent on the morphology of explosives and the interaction of solvent with explosives. Among the many computational methods, molecular dynamics (MD) simulation is a powerful approach for investigating the mechanism of crystallization, because it could give us atomic-scale information. And many studies on crystal growth simulation using the MD method have been reported [4–7].

In recent years, the studies on 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) have become one of the hotspots in insensitive explosive researches. The structure of ANPyO is similar to that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), making it potential insensitive high energy explosive candidate with heat resistance, low mechanical and thermal sensitivity [8]. Ritter and Licht reported the synthesis of ANPyO by the nitration of 2,6-diaminopyridine followed by oxidation using H_2O_2 in acetic acid [9]. However, the method has the disadvantages of low yields, high impurity contents and high danger coefficient. Some researchers focused on the improvement of synthesis of ANPyO [10–12].

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Compared with experimental studies, few theoretical researches on ANPyO have been done [13–16]. Liu et al. performed a periodic DFT calculation of ANPyO to obtain its optimized structure, the insight into the chemical properties and the theoretical lattice energy of the crystal [13]. The work of Ju et al. was trying to investigate theoretically the structures and the binding energies of the ANPyO dimers by first-principle methods [14]. However, the studies which have been done at the molecular level before were unconcerned with the effect of solvents on the morphology of ANPyO. ANPyO possesses symmetrical molecular structure and exhibits strong chemical stability, resulting in a low solubility or insolubility in common organic solvents, therefore, the annealed solvents used for ammonium nitrate explosives are not generally suitable for ANPyO. According to the previous study [12], trifluoroacetic acid was chosen as solvent for ANPyO recrystallization in this study, and MD simulations were carried out for the first time to explore the morphology modification of ANPyO induced by solvent. In addition, we also performed the diffusion coefficients calculation of trifluoroacetic acid molecules on the habit crystal faces to probe the effect of stirring on the crystal growth of ANPyO. This provides the fundamental information on the potential morphological changes in the stage of the design of a crystallization process.

2. Theories and MD simulation details

2.1. Attachment energy model

The growth morphology algorithm is based on the attachment energy (AE) method and can predict the shape of a crystal more accurately than the BFDH method because it takes the energetics of the system into account. The AE model was proposed by Hartman and Bennema based upon period bond chain (PBC) theory [17]. The AE method attempts to simulate crystal habits as obtained under non-equilibrium growth conditions. It relates the relative growth rate of a given surface to the potential energy per unit cell gained if a new layer of material attaches to the surface in vacuum.

The attachment energy, E_{att}, is defined as the energy released on attachment of a growth slice to a growing crystal surface. E_{att} is computed as [18]:

$$E_{att} = E_{latt} - E_{slice} \quad (1)$$

where E_{latt} is the lattice energy of the crystal, E_{slice} is the energy of a growth slice of thickness d_{hkl}. The relative growth rate in vacuum of the crystal surface, R_{hkl}, is assumed to be proportional to the absolute value of attachment energy:

$$R_{hkl} \propto \left| E_{att} \right| \quad (2)$$

In other words, the crystal surfaces with smaller absolute value of the attachment energies grow slower and, therefore, are more morphologically important.

2.2. Simulation details

All calculations were performed using the program Materials Studio 3.0 (Accelrys Inc., USA) [19]. The initial structure of ANPyO unit cell was taken from the experiment by Hollins et al. [20], which crystallized in the monoclinic space group of *C2/c* with five independent lattice parameters $a = 14.864$ Å, $b = 7.336$ Å, $c = 7.509$ Å, $\alpha = \gamma = 90^\circ$, and $\beta = 111.67^\circ$. There are two irreducible molecules in the unit cell, and the model was built with Visualizer module and the optimization of the unit cell was performed in the COMPASS force field [21].

The AE model was used to predict the crystal morphology of ANPyO in vacuum, acquiring the main stable crystal faces with different Miller indices (*h k l*). Then, the ANPyO crystal was cleaved along the main stable faces (1 1 0), (1 0 0), (1 0 −1) and (1 1 −2), which were extended to 3D periodic superstructures of 2.253 nm × 2.486 nm × 3.633 nm, 2.201 nm × 2.253 nm × 3.460 nm, 2.934 nm × 2.792 nm × 2.915 nm, and 2.768 nm × 3.315 nm × 3.189 nm, respectively. The (1 1 0) and (1 0 0) super cells include 54 ANPyO molecules (1080 atoms in total) while the (1 0 −1) and (1 1 −2) super cells consist of 64 ANPyO molecules (1280 atoms in total). A solvent layer filled with 1 0 0 random distributed trifluoroacetic acid molecules was built with the layer density set to be 1.535 g/cm^3 by the Amorphous Cell tool. Geometry optimization, followed by MD simulations (1 0 0 ps with time step 1 fs at 288 K, using the Andersen thermostat [22]) for the solvent layer was done to make trifluoroacetic acid molecules uniformly distribute in the solvent layer.

In order to investigate the effect of solvent on the crystal morphology, the interfacial model was employed, which is composed of an ANPyO crystal layer and a trifluoroacetic acid solvent layer. In the study, the solvent layer was adsorbed on the (*h k l*) crystal face along c axis. A vacuum slab thickness of 20 Å was built above the solvent layer to eliminate the effect of additional free boundaries on the structure. The crystal layer was constrained along *a*, *b*, and *c* axis directions during the MD simulation process. The schematic view of the starting conformations for ANPyO face–trifluoroacetic acid solvent interfacial models is shown in Fig. 1.

The energy minimization for the interfacial model was carried out using a molecular mechanic method (MM) before the MD simulations, which were carried out using the Discover module in Materials Studio along with the use of COMPASS force field [21]. The COMPASS force field is a powerful *ab initio* force field which has been parameterized and validated using condensed phase properties, in addition to various *ab initio* and empirical data for molecules in isolation. Consequently, this force field enables the accurate and simultaneous prediction of structural, conformational, vibrational, and thermophysical properties for a broad range of molecules in isolation or condensed phases under a wide range of conditions of temperature and pressure [23,24].

All MD simulations were carried out at 288 K in the NVT ensemble [25]. The coupling to the heating bath was carried out using the Nose thermostat [26]. MD simulation was started by taking initial velocities from a Maxwell distribution. The solution to Newton′s Laws of Motion was based on assumptions as follows: periodic boundary condition and time average is equivalent to the ensemble average. Integral summation was carried out with a Verlet velocity integrator [27]. The nonbonding interactions in each system, as well as the Van der Waals force and electrostatic force were computed using an atom-based summation method and the Ewald summation method, respectively, with a cutoff radius of 0.95 nm (spline width: 0.10 nm; buffer width: 0.05 nm). When any interaction pair moves more than half this distance, the neighbor list is recreated. Tail corrections were used to calculate the potential energy contributions from interactions between atoms separated by distances longer than the nonbonding cutoff. The time step was set to 1 fs, equilibration stage ran for 200,000 fs, and then the production stage ran for 300,000 fs, the data were collected for subsequent analysis at the same time. The trajectory was recorded every 500 fs.

3. Results and discussion

3.1. ANPyO crystal morphology in vacuum

Fig. 2 shows the crystal morphology of ANPyO in vacuum calculated by the AE model using Forcefield assigned charges and the Compass force field, and Table 1 lists the relevant parameters of the main crystal habit faces of ANPyO.