ON PREDICTING THE CRYSTAL STRUCTURE OF ENERGETIC MATERIALS FROM QUANTUM MECHANICS

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ABSTRACT

A quantum-mechanically-based potential energy function that describes interactions of dimers of the explosive cyclotrimethylenetrinitramine (RDX) is used to predict polymorphic structures of crystalline RDX. The potential was first used in crystal structure prediction methods which generate polymorphs of RDX and provide a 0 K ordering in energy. The 13 low energy-structures generated by crystal structure prediction methods were subsequently subjected to isothermal-isostress molecular dynamics (N*s*T MD) simulations to establish stability rankings and assess effect of inclusion of temperature. For both crystal structure prediction methods and molecular dynamics simulations, the low-energy polymorph corresponds to the experimental structure with crystallographic parameters in outstanding agreement with experiment.

1. INTRODUCTION

Advances in quantum mechanical methods and computational resources have allowed ARL researchers to develop powerful predictive capabilities for use in the design and development of advanced energetic materials. These computational tools are used to predict properties of energetic materials related to performance or hazard, thus allowing for assessment of a notional material using computational methods only. One key property is the crystal density; we have expended considerable effort in developing a robust capability for its prediction using theoretical information only.

Although the molecular structure of single molecules can be easily and accurately predicted using highly-accurate quantum mechanical (QM) methods, the same cannot be said for predicting the system in its crystalline state. In fact, prediction of a crystal structure using information only about the atomic arrangement of a constituent molecule was once considered impossible [Dunitz, 2003] due to substantial theoretical and computational challenges, including properly representing the dominant binding forces within molecular crystals, van der Waals interactions. While these forces can be modeled *ab initio* by wave-based methods of quantum chemistry, the high computational cost of such approaches has prevented extensive applications of these methods to molecular crystals. The only computationally-feasible quantum-mechanically-based approach to treat molecular crystals is Density Functional Theory (DFT), shown to be inaccurate for systems for which van der Waals forces are dominant (e.g. molecular crystals) [Byrd et al., 2004].

These computational restrictions have, to this point, forced us to include empirical models in methods for prediction of crystal structures. These empirical models rely on experimental information for parameterization and are limited in their predictive capability. To illustrate, in a previous study, we used a molecular simulation approach that allows for the *a priori* prediction of the crystal density and crystallographic parameters using information about a single molecule (i.e. *ab initio* crystal prediction*)*; however, the intermolecular interactions were described by this empirical potential [Rice and Sorescu, 2004]. A total of 174 CHNO molecular crystals for which experimental crystallographic information is available were subjected to this approach. The calculations produced 148 crystals whose crystallographic parameters and molecular configurations matched those of the experimental counterpart. Unfortunately, the method and potential failed to identify 26 of the structures. Subsequent application of the method and model to high-nitrogen molecular crystals was completely unsuccessful. These failures demonstrate that atomistic simulations using empirical models often produce unsatisfactory results in describing systems outside of those included in the fitting data.

Here we provide an alternative approach to such empirical modeling and demonstrate it for the well-known energetic material, cyclotrimethylenetrinitramine (RDX). The potential energy function for describing crystalline RDX is based on dimer interactions calculated using a highly accurate quantum mechanical method, symmetry-

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adapted perturbation theory based on the density-functional description of the monomers [SAPT(DFT)] [Podeswa et al, 2007]. In order to establish the quality of the SAPT(DFT)-based potential and its utility for use in molecular simulations of condensed phase RDX, we subjected it to a series of increasingly rigorous atomistic simulations to determine its suitability for use, its deficiencies and its limitations. As a first step in such an assessment, we used it to model crystalline RDX at ambient conditions using isothermal-isostress molecular dynamics (NsT-MD) simulations assuming as an initial configuration the structure of the experimental crystal. Subsequent tests included generation and energy ranking of polymorphs, and subsequent subjection of the polymorphs to NsT-MD simulations for energy ranking when thermal motion is included.

2. COMPUTATIONAL DETAILS

A complete, six-dimensional potential energy surface (PES) describing interactions between dimers of RDX was generated using over 1000 single-point calculations using the SAPT(DFT) method [Misquitta et al, 2005]. A functional form of the potential energy surface assumed a site-site formulate over all nuclei of a pair of dimers, and was fitted to the SAPT(DFT) points. Details of the calculations and the fitting are given in [Podeswa et al, 2007]. Before subjecting the PES to polymorphic crystal structure prediction, we used it in isothermal-isostress molecular dynamics (NsT-MD) simulations using the experimentally determined crystal as the initial state.

Polymorphic crystal structures corresponding to local minima on the PES were identified using the method of *ab initio* crystal prediction as implemented by Ammon and co-workers [Holden et al., 1993] in the MOLPAK/WMIN suite of crystal prediction software. The MOLPAK/WMIN procedure is similar to those of most *ab initio* crystal prediction methods, which generally consists of three steps, with the first step corresponding to generating a three-dimensional model of the molecule that will be used to construct candidate crystals of different symmetries (denoted hereafter as the "test molecule"). Although quantum mechanical procedures can reliably and rapidly predict geometries of the model used in this first step, the three-dimensional model we used corresponds to the experimental structure at room conditions [Choi and Prince, 1972] since this was the configuration used for the generation of the SAPT-DFT points to which the PES was fitted.

The second step of the procedure involves creating hypothetical crystal structures using the molecular models. In the MOLPAK procedure, an initial packing arrangement is obtained by surrounding the test molecule with a coordination sphere containing other molecules. The contents and three-dimensional structure of the sphere are dependent on the crystalline space group symmetry. The definitions of the various coordination spheres used in a MOLPAK calculation were obtained from detailed analyses for a large number of organic crystal structures [Holden et al., 1993]. The analyses showed that the most probable number of molecules in the coordination sphere is 14, and that specific "patterns and sub-patterns" were apparent in the three-dimensional structure of the coordination spheres (Holden et al., 1993). The version of MOLPAK used in this study samples 51 coordination groups corresponding to the triclinic (P1, P$\bar{1}$), monoclinic (P2_1, P2_1/c, Cc, C2, C2/c, Pc, P2/c, P2_1/m, P2/m, P2, Pm, P2/m), and orthorhombic (Z=4, P2_12_12, P$2_12_12_1$, Pca2_1, Pna2_1, Pnn2, Pba2, Pnc2, P22$2_1$, Pmn2_1, Pma2, Z=8, Pbcn, Pbca) space groups.

Adjacent molecules in the initial coordination sphere are then systematically moved in small steps toward the centrally-located test molecule. At each step, the potential energy of the "crystal" is calculated. This continues until a repulsion criterion is met. Once this criterion is met, the packing procedure stops, and the volume, crystallographic parameters and Eulerian angles that describe the orientation of the test molecule are stored.

Next, a new candidate crystal is generated by first reorienting the test molecule about only one of the Eulerian axes by 10°, and repeating the packing procedure described heretofore until the entire Eulerian space is sampled. Rotations in 10° steps about the three Eulerian axes will result in the generation of 6,859 (19^3) orientations and hypothetical crystal structures for each of the possible space group/coordination sphere combinations.

After the ~7000 structures were generated for each coordination sphere geometry, they are ranked according to density. The 500 most dense structures are subjected to full energy minimization, where minimization is performed with respect to the crystallographic parameters. The energy minimization is space-group symmetry restricted (i.e., the space group symmetry is conserved throughout the minimization), and performed using the code WMIN [Busing, 1981].

At the completion of the energy minimizations of the 500 most dense hypothetical crystals generated for each of the 51 space group/coordination-sphere geometries, the user has the information needed to identify the "correct" crystal structure according to his specific criteria (e.g. lowest lattice energy or highest density [Lommerse et al., 2000]). For our purposes, we have ranked the crystals according to lowest lattice energy.

The MOLPAK/WMIN procedure proceeds under the assumption that all important regions of configuration space are adequately sampled and that the interatomic interactions are sufficiently accurate to describe packing and lattice energies.

Due to limitations in the MOLPAK/WMIN software, a scaled down version of the SAPT(DFT) potential was used in the prediction of the polymorphs; its form is a standard pair additive exponential six form with coulombic interactions, required by our version of the MOLPAK/WMIN software. It will be denoted hereafter as the SAPT(DFT)$_{\text{exp-6}}$ potential. While this modified version of the PES was utilized in the polymorph predictions, its features were compared with those of the full SAPT(DFT) potential, and showed only minor differences in most cases. We checked this by performing one isothermal-isostress molecular dynamics (N*s*T MD) simulation] on the low-energy polymorph with both potentials: The cell vectors of the time-averaged geometry differed by no more than 0.7% in the two cases.

The 13 lowest-energy cells generated through the WMIN optimization are then used as initial structures in N*s*T-MD simulations to determine stability and energy ranking relative to the experimental structure. For the N*s*T-MD simulations, the full SAPT(DFT) PES was used. The rigid-molecule approximation was assumed and no symmetry constraints were imposed during the trajectory integration. The DL_POLY version 2 suite of molecular dynamics software was used, with thermostat and barostat relaxation times set at 2.0 and 5.0 ps, respectively. Supercells for the polymorphs consisted of blocks of unit cells, with sizes selected to ensure that the perpendicular widths between opposing faces of the simulation cell were at least twice the interaction potential cutoff distance (12.0 Å). Coulombic interactions were handled using Ewald summations. Atomic velocities corresponding to T=300 K were then assigned and a trajectory of 30,000 steps (1 time step = 0.001 fs) was performed to equilibrate the system. During equilibration, atomic velocities were scaled at every fifth step to more quickly drive the system to the target temperature.

After equilibration, time-averaged thermodynamic properties and crystal parameters were determined from results of 100,000-step N*s*T-MD trajectory. Also, at every 500th step during the trajectory, atomic configurations were recorded to generate time-averaged information about the contents of the simulation cell. Results are given in terms of center-of-mass fractional (s_x,s_y,s_z) and the Euler angles ($\theta.\phi,\psi$) that transform the principal axes of inertia of each molecule to its space-fixed coordinate system (i.e., the Cartesian axes). For each polymorphic form studied, the molecular parameters for each of the symmetry-equivalent molecules in the unit cell were averaged over time and over all unit cells within the simulation supercell.

A key test of an intermolecular interaction potential to describe molecular crystals it is ability to maintain the proper crystalline space group symmetry during N*s*T-MD simulations at the appropriate temperature and pressure. We assessed whether such was maintained during the trajectories by generating “ideal” unit cells for the 13 polymorphs subjected to N*s*T-MD simulation. Each ideal cell was constructed using the time-averaged atomic positions of one of the molecules in the simulation cell, and generating the appropriate number of symmetry equivalents required to construct a unit cell according to the space group symmetry requirements. The molecular parameters (center-of-mass fractionals and orientational Euler angles) of the time-averaged unit cells generated from the N*s*T-MD simulations were then compared with those of the ideal crystals.

3. RESULTS AND DISCUSSION

3.1 SAPT(DFT)-based PES

In the SAPT(DFT) method, the interaction energy can be decomposed into components, each of which has a clear physical interpretation and describe various interactions, including electrostatic, exchange, induction, exchange-induction, dispersion, and exchange-dispersion interactions. These calculations represent the largest system ever investigated with any high-level electronic structure method. 51 local minima were identified on the PES for this system; each was analyzed in terms of the physical components of the interaction energy. As expected, the dispersion represented the dominant component, although in some cases, the electrostatic interaction is significant. The analysis of the SAPT(DFT) PES indicates that the neglect of the dispersion contribution would result in excessively weakly-bound (or unbound) dimers. This analysis provides a definitive explanation as to why conventional DFT treatments (which do not properly treat dispersion) provide inaccurate descriptions of crystalline RDX.

As a first step in assessing the utility of this PES for use in molecular simulations of crystalline RDX, an N*s*T-MD simulation of the experimental crystal structure at room conditions was performed. The resulting crystallographic parameters and orientations of the molecules within the unit cell were in excellent agreement with experiment. Figure 1 shows the superposition of the predicted unit cell onto the experimental one. The agreement with experiment is excellent, even better than typically achieved in simulations with empirical potentials fitted to a given set of crystal data.

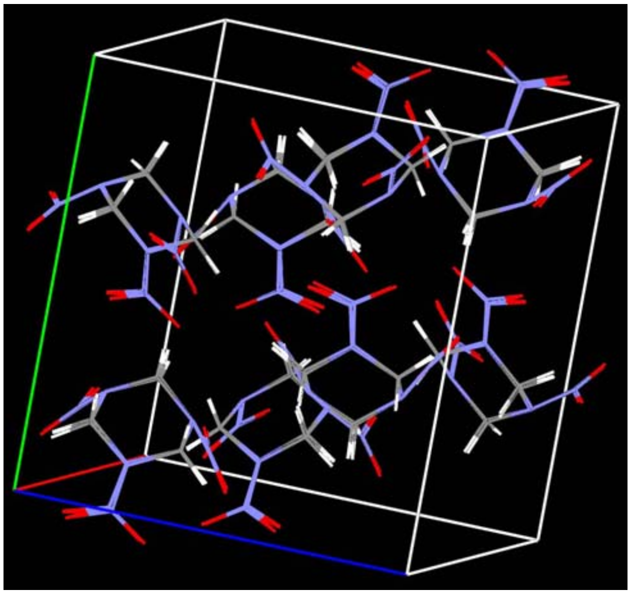

Figure 1. The predicted RDX unit cell superimposed onto the experimental structure.

3.2. Prediction of RDX Polymorphs

MOLPAK/WMIN predictions of the density and lattice energy (per molecule) for the low energy crystal for each of the 51 coordination groups sampled in this study were performed, with the lowest energy crystals corresponding to the Pbca, P2$_1$/c, P2$_1$2$_1$2$_1$, Pna2$_1$, and C2/c crystalline space groups. The low energy crystal, corresponding to Pbca (the experimental space group), is lower in energy by at least 1.94 kcal/mol than all other crystals, thus eliminating any ambiguity in the polymorph ranking. Of the thirteen polymorphs identified by the MOLPAK/WMIN procedure and subsequently subjected to N*s*T-MD simulation, one produced an amorphous structure upon introducing thermal and dynamic motion; this corresponded to MOLPAK/WMIN Solution 444, coordination group AK (space group P2$_1$/c). This indicates that the MOLPAK/WMIN SAPT(DFT)$_{\text{exp-6}}$ structure is not a stable minimum on the SAPT(DFT) PES. No further analysis of this structure was performed.

Deviations of the N*s*T-MD results from those of the MOLPAK/WMIN predictions were no greater than 5.6% in cell dimension, 1.3° in cell angle, and 8% in density. A more rigorous comparison of the contents of the cells generated through N*s*T-MD simulations and MOLPAK/WMIN calculations are performed through superposition of the N*s*T-MD time averaged unit cells onto the MOLPAK/WMIN counterpart as described in Rice and Sorescu [2004]. The maximum rigid-body rotational displacement and translational displacement of any of the symmetry-equivalent molecules in the time-averaged unit cell relative to those of the MOLPAK/WMIN counterpart were 16.3° and 0.58 Å, respectively. However, these values corresponded to higher-energy polymorphs. Among the four lowest-energy polymorphs, the maximum rigid-body rotational displacement and translational displacement of any of the symmetry-equivalent molecules in the time-averaged unit cell relative to those of the MOLPAK/WMIN counterpart are 8.7° and 0.30 Å, respectively.

The N*s*T-MD lattice energies are all higher than the MOLPAK/WMIN results but the densities are consistently lower. These trends can be partially attributed to thermal effects introduced in the MD simulations, whereas the MOLPAK/WMIN calculations represent a 0 K result; thermal expansion should generate lower densities and higher lattice energies. Also, there are slight differences in absolute energies between the SAPT(DFT)$_{\text{exp-6}}$ and SAPT(DFT) potentials, resulting in differing relative energy rankings of the MOLPAK/WMIN and N*s*T-MD structures. However, for both sets of calculation, the low-energy structure corresponds to the experimental crystal.

Table 1 provides the time-averaged crystallographic parameters for the 4 lowest-energy crystals produced from N*s*T-MD simulations using the SAPT(DFT) potential.

Table 1: Crystallographic parameters calculated using N*s*T-MD/SAPT(DFT) methods.

Solution/Space Group	***a* (Å)**	***b* (Å)**	***c* (Å)**
Experiment	13.82	11.574	10.709
CB-4/ Pbca	13.234	11.609	10.720
CB17/Pbca	13.377	11.682	10.755
AM17/P2$_1$/c	8.132	10.702	9.662
AM75/P2$_1$/c	7.236	11.683	10.719
Solution/Space Group	**α (°)**	**β (°)**	**γ (°)**
Experiment	90.00	90.00	90.00
CB-4/ Pbca	90.00	89.99	90.00
CB17/Pbca	90.00	89.99	90.00
AM17/P2$_1$/c	90.00	96.41	89.99
AM75/P2$_1$/c	90.00	71.46	90.00

The initial configurations for the MD simulations were generated from calculations using the MOLPAK/WMIN procedure and the SAPT(DFT)$_{\text{exp-6}}$ potential. Table 2 provides the maximum deviations of the monomer's positions and orientations in the time-averaged unit cells from those of the "ideal" RDX crystals for each of the four low-energy polymorphs. Of the 13 crystals subjected to N*s*T-MD simulations, the maximum deviation of center-of-mass fractional coordinates from ideality among all of the polymorphs is 0.0032 fractional units (Solution 75, AM) and the maximum deviation of Euler angles from ideality is 3.01° (Solution 304, AK). The good agreement of the N*s*T-MD averaged values with those of "ideal" crystals demonstrate that the crystalline space group symmetries are well maintained throughout the simulations for these polymorphs. Values in Tables 1 and 2 are given in order of increasing lattice energy, with crystal CB-4/Pbca having the lowest lattice energy.

Table 2: Maximum absolute deviations of monomers' positions and orientations from corresponding values in an ideal RDX crystal.

Solution/Space Group	Δsx_{Max}	Δsy_{Max}	Δsz_{Max}
CB-4/ Pbca	3.1e-04	2.5e-04	1.9e-04
CB17/Pbca	2.3e-04	5.2e-04	3.0e-04
AM17/P2$_1$/c	6.8e-04	2.5e-04	2.4e-04
AM75/P2$_1$/c	3.2e-03	1.8e-04	7.8e-04
Solution/Space Group	$\Delta\Theta_{\text{Max}}$ (°)	$\Delta\Phi_{\text{Max}}$ (°)	$\Delta\Psi_{\text{Max}}$ (°)
CB-4/ Pbca	0.16	0.07	0.13
CB17/Pbca	0.13	0.14	0.12
AM17/P2$_1$/c	0.19	0.64	0.97
AM75/P2$_1$/c	0.34	0.02	0.97

Lattice parameters for the experimental crystal are also given in Table 1 for comparison with the low-energy time-averaged structure (Solution CB-4) generated in the N*s*T-MD simulations. Note that the predicted low-energy structure has the same space group as the experimental crystal. Agreement with experiment for all cell parameters is very good. The deviations from experiment of the N*s*T-MD densities and cell edge lengths in the *a*-, *b*- and *c*- directions are -0.8%, 0.4%, 0.3%, and 0.1%, respectively. A comparison of time-averaged center-of-mass fractional coordinates and orientational Euler angles for the eight symmetry equivalent molecules in the unit cell with corresponding experimental values for RDX at 298 K, 1 atm, showed outstanding agreement. The largest deviation in molecular orientation occurs for the Euler angle ψ, which differs from experiment by ~2.7°. Also, the largest deviation of the location of the molecular mass center is less than 0.07 Å.

In order to estimate the uncertainties of the SAPT(DFT) PES, we evaluated the main neglected component, the non-additive three-body contributions to the lattice energy for the experimental geometry of the crystal, which is the main component of the energy that was neglected in these calculations. This contains the HF energy (0.76 kcal/mol), the dispersion energy (1.00 kcal/mol), and the leading asymptotic dispersion term (0.31 kcal/mol). These values were obtained using 28, 7, and ~ 8 x 10^6 symmetry-unique trimers. Since these three-body contributions are small relative to the two-body component, the lattice parameters should change very little upon their inclusion in the PES. Additionally, the total three-body effect is dominated by the dispersion energy, which is fairly isotropic and would be similar for all of the polymorphs. Thus, we conclude that the relative energies of the polymorphs are unlikely to change after including the many-body forces. The absolute value of the lattice energy changes by 6.7% for structure CB/4, suggesting that the good agreement of the pairwise additive energy with experiment is due to a cancellation of errors, including basis set incompleteness error of the pair potential countermanded by the three-body effects of opposite sign.

CONCLUSIONS

We have demonstrated that the SAPT (DFT) method is capable of producing force fields for interactions of the molecular crystalline explosive RDX, and appears to be suitable to enable reliable predictions of crystal structures of similar molecular crystalline compounds. The predictions were done entirely from first principles, with no reliance on empiricism, thus demonstrating that compounds for which experimental data are unavailable can be explored using theoretical simulation methodologies. We expect this method to find broad applications not just in energetic materials design and development, but also in areas of crystal design, in particular, to screening novel materials and drug candidates, screening molecules for co-crystallization, and identification of low-energy polymorphs of pharmaceutical compounds.

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