J. At. Mol. Sci.
doi: 10.4208/jams.032811.051411a

Vol. 3, No. 1, pp. 41-48
February 2012

# Properties and phase transitions of the solid $\beta$-HMX: different force fields

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Received 28 March 2011; Accepted (in revised version) 14 May 2011

**Abstract.** The structure, cell volume and lattice constants of $\beta$-octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine ($\beta$-HMX) crystal are studied by using the classical molecular dynamics method. The variations of cell volume and lattice constants are presented and discussed under different pressures and temperatures. The main purpose of the present work is to understand effect of different force fields, the CVFF and PCFF force fields were used instead of usual COMPASS. It is found that the cell volume is less satisfactory, and there was an abrupt change at 370 K and 440 K for the lattice constants and cell volume with CVFF force field. However, for PCFF force field, an abrupt change occurred at 360 K and 430 K, respectively. It means that $\beta$-HMX may have phase transitions at these temperatures in accordance with experimental observation. It is suggested that selection of suitable force field play an important role in achieving desired accuracy of simulation results.

**PACS**: 71.15.Mb
**Key words**: $\beta$-HMX crystal, molecular dynamics, force fields, phase transitions

## 1 Introduction

The high explosive octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) which also referred to as high melting explosive is a typical energetic material and one of the most potent chem-

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*Corresponding author. *Email address:* `dqwei@sjtu.edu.cn` (D. Q. Wei) ical explosives manufactured. It have been widely used in the polymer bonded explosives (PBXs) and propellant formulation [1]. HMX is an achromatous crystal and exhibits four pure crystal polymorphs at ambient pressure, namely $\alpha$-HMX, $\beta$-HMX, $\gamma$-HMX and $\delta$-HMX [2]. The stabilities of these polymorphs are known to be $\beta<\alpha<\gamma<\delta$ at ambient conditions [3]. Although the stability field of these phases at high pressures and temperatures are not very clear, the $\beta$ phase is considered the most stable phase at high pressures at least to 10 GPa [4, 5]. Also, it crystallizes into the monoclinic space group $P2_{1/c}$ according to x-ray [6] and neutron experiments, with the crystal lattice $a=6.54$ Å, $b=11.05$ Å, $c=8.70$ Å, $\beta=124.3°$. The $\beta$ phase has a monoclinic $P2_{1/c}$ structure with two $C_4H_8N_8O_8$ molecules per unit cell at ambient conditions [7] and transforms to the $\delta$ phase at 165–210 $°C$ at ambient pressure [8]. The unit cell and single molecular structure of $\beta$-HMX in the crystal phase obtained from geometry optimization was shown in Fig. 1. It can be seen that each $C_4H_8N_8O_8$ molecule involves two $NO_2$ groups above and two below the ring plane, and there is a central ring having eight atoms for N or C across. The $\alpha$-phase crystal structure was reported to be stable in the temperature range 376–435 K [2] with the orthorhombic symmetry (space group Fdd2) and has eight molecules in the unit cell. The $\delta$-polymorph belongs to the hexagonal symmetry with space group $P6_1$ and $Z=6$ molecules per unit cell, and stable above 433 K up to the melting point 553 K. Each $C_4H_8N_8O_8$ molecule in $\alpha$-and $\delta$-phase is in so called "boat" conformation, having all four $NO_2$ groups on the same side of the ring plane.

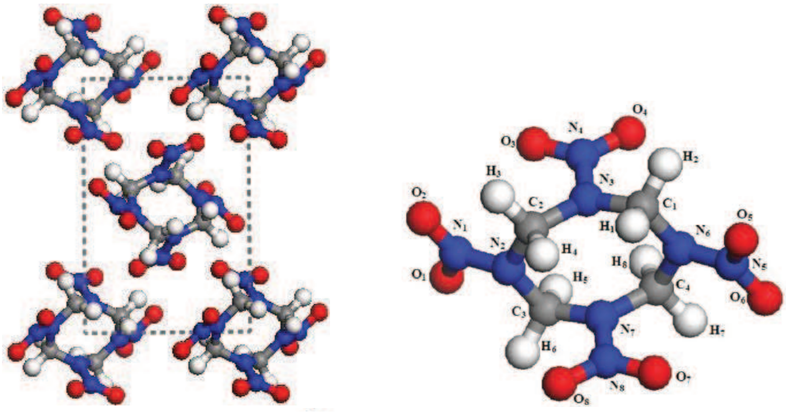


Figure 1: Unit cell of the $\beta$-HMX crystal (left) and the molecular structure (right), where C: Gray, N: blue, O: red, H: white.

Dan *et al.* [9] performed the isothermal-isobaric molecular dynamics (NPT-MD) simulations of the $\beta$, $\alpha$, and $\delta$ phases of HMX over the temperature range 4.2–553 K and 1 atm. The predicted space group symmetries and structural parameters for the three phases of HMX are in close agreement with experimental values. Choong-Shik *et al.* [10] investigated $\beta$-HMX at high pressures and temperatures by using a DAC coupled with micro-Raman spectroscopy and angle-resolved x-ray diffraction using an intense monochromatic synchrotron beam and image-plate detectors. Their main results include: (i) isotherms of HMX obtained in both hydrostatic and nonhydrostatic conditions; (ii) chemical reactions of HMX in nonhydrostatic conditions; (iii) the evidence for the phase transitions of HMX in hydrostatic conditions at 12 and 27 GPa. Yu *et al.* [11] used the CHARMM program to study HMX. In their simulations, three types of simulations with different conditions were performed to investigate the effect of the crystalline state on the decomposition processes of the molecule. Their molecular orbital studies showed that the compressed N–N bonds in the crystals play an important role in the initial decomposition processes of the nitramine which is induced by strong physical stimulate such as impact.

In this paper, we studied the basic properties (such as the crystal structure, cell volume and lattice constants) of $\beta$-HMX under high temperature and high pressure using CVFF and PCFF force field, respectively. The purpose is to validate whether the accuracy of the simulation results rest with the selection of force field. The rest of this paper is organized as follows: in Section 2, we introduce the computational methods simply. The detailed description and analysis of our results are presented in Section 3. Finally, a conclusion of the present study is given in Section 4.

## 2 Computational methods

The MD simulations are performed in the isothermal-isobaric (NPT) statistical ensemble [12] using DISCOVER [13, 14] module in the Materials Studio software package in the similar fashion of previous studies of HMX [15–17]. The present works is performed using two force fields, i.e., CVFF and PCFF. The constant pressure and temperature (NPT) simulations are carried out using the Andersen thermostat and Berendsen [18] pressure control methods. Our MD simulation boxes contain $4\times2\times3$ crystallographic unit cells with 48 molecules, which is so chosen to ensure the use of a cutoff distance for the intermolecular potentials about 10.5 Å. The periodic boundary conditions corresponding to a triclinic primary cell were used. A fixed time step size of one femtosecond (1 fs$=1\times10^{-15}$ s) was used in all cases. The systems were sampled with the total integration time of 50000 time steps, of which 20000 steps were equilibration; the next 30000 integration steps are collected for subsequent analysis. The velocities are scaled every 50 steps. The initialization temperature and pressure is 5 K and 0 GPa and the initialization structure is the experimental one [8].

## 3 Results and discussion

### 3.1 The crystal properties at ambient conditions

Determining the lattice constants of the molecular crystals at ambient conditions are important not only to know the molecular crystal structure before the compression starts, but also to benchmark the performance of the theoretical methods for its ability to describe the intermolecular interactions. The computed lattice constants and unit cell volume of the $\beta$-HMX

Table 1: The experimental and theoretical lattice constants $a$,$b$,$c$ (Å), unit cell volumes $V$ (Å$^3$), crystal angle $\beta$ (deg) and density $\rho$ (g/cm$^3$) of $\beta$-HMX.

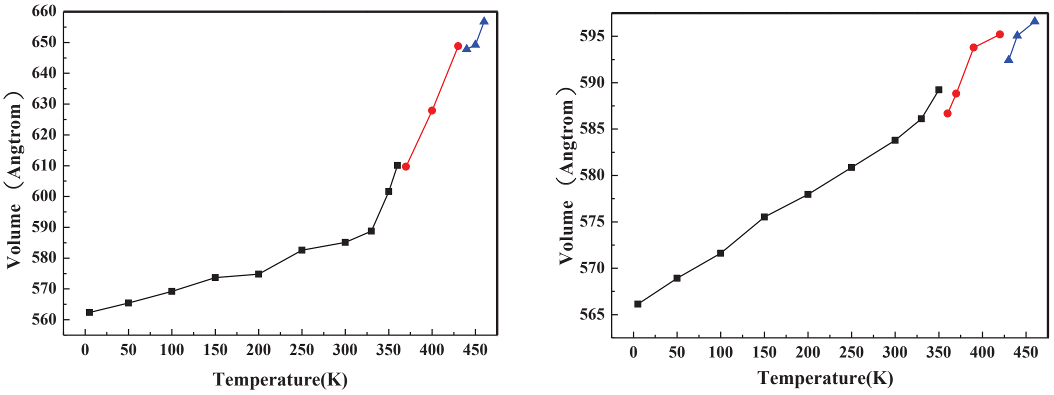
| | CVFF | PCFF | COMPASS [19] | CHARMM [11] | Experiment [7] |
|---|---|---|---|---|---|
| $a$ | 6.22 | 6.29 | 6.57 | 6.53 | 6.54 |
| $b$ | 11.20 | 13.12 | 10.63 | 11.05 | 11.05 |
| $c$ | 9.99 | 8.24 | 9.13 | 7.35 | 8.70 |
| $V$ | 587.25 | 584.41 | 530.60 | 517.20 | 519.39 |
| $\beta$ | 122.72 | 120.57 | 123.67 | 102.69 | 124.30 |
| $\rho$ | 1.681 | 1.685 | | | 1.902 |

crystal at 0 GPa and 300 K are compared with the experimental data [10, 11] and previous theoretical results [16] as shown in Table 1.

From Table 1, it is found that compared to the experimental results, our calculations underestimate lattice constant $a$ and $\rho$ by 4.89% and 11.62%, and overestimate $b$ and $c$ by 1.36% and 14.83%, respectively using CVFF force field. However, PCFF force field underestimates $a$, $c$ and $\rho$ by 3.82%, 5.29% and 11.41%, but overestimate b by 18.73%, respectively. Apparently, it is not as good as results from the COMPASS force field and other force field parameters in the previous theoretical studies [16–23].

## 3.2 The structural properties at different temperatures

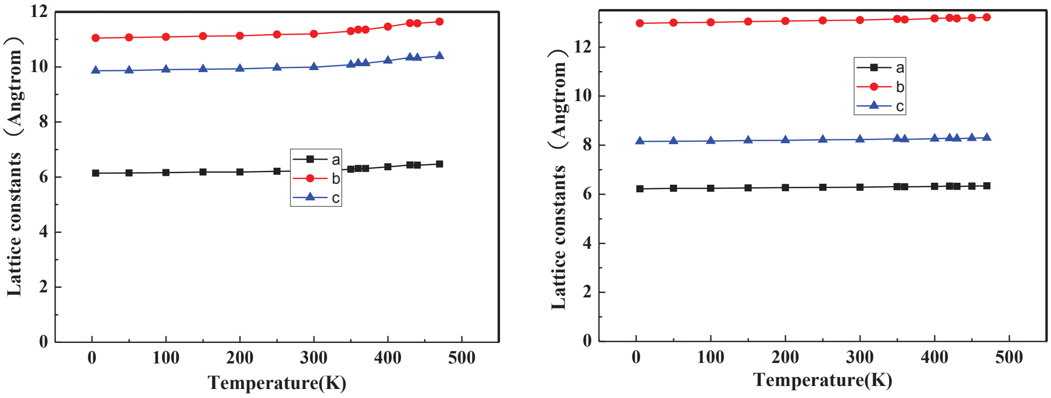
The properties of $\beta$-HMX at different temperatures are obtained at 0 GPa and the temperature is from 5 K gradually increased to 470 K by an increment of 50 K. The unit cell volume and the lattice constants of $\beta$-HMX obtained by the CVFF and PCFF force field calculations versus temperature are plotted in Fig. 2(a)–(b) and Fig. 3(a)–(b), respectively.



(a) (b)

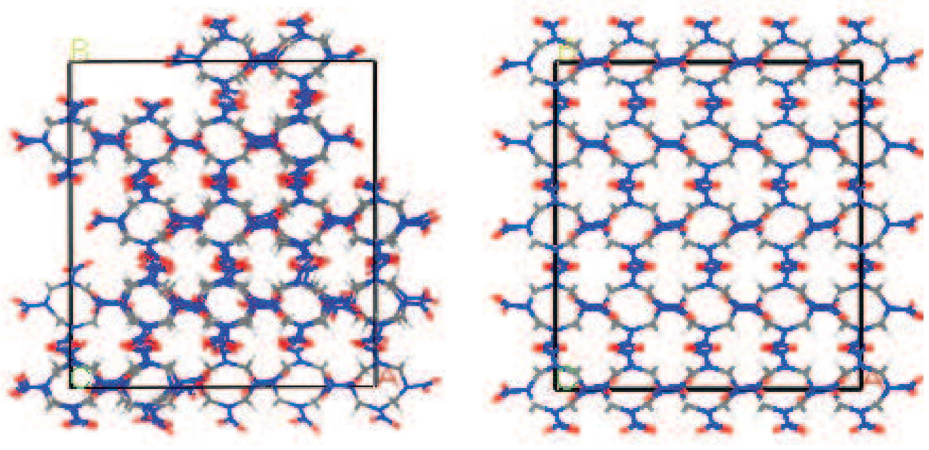
Figure 2: Temperature dependence of the unit cell volume. (a) the CVFF force field (b) the PCFF force field.

From Fig. 2(a), it is shown that the unit cell volume increases slowly from 5 K to 350 K, but takes off at 350 K. It exhibits two discontuities at 370 K and 440 K, respectively. From Fig. 2(b), we also observe the same general trend, and the abrupt changes in volume are seen at 360 K and 430 K, respectively. It implies that the $\beta$-HMX crystal has phase transitions at these temperatures, which is supported by experimental data [24]. From Fig. 3(a), it is seen that the lattice constants increase with temperature but less rapidly as the unit cell volume in Fig. 2. Even the phase transitions are not really evident with the scale of Fig. 3. As the experiment shows, the lattice expansion is highly anisotropic with the largest length change along the $b$. In order to understand the structure changes when the phase transitions occur, we show the crystal structures before and after the phase transitions in Fig. 4.

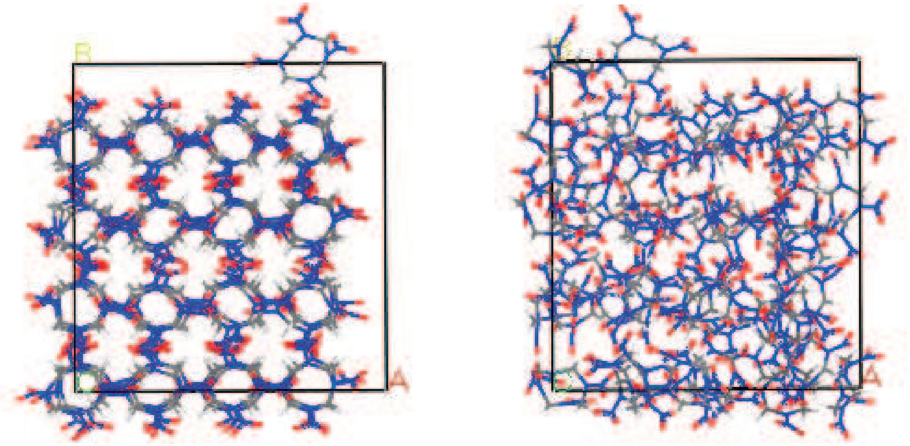


(a) (b)

Figure 3: Temperature dependence of the lattice constants. (a) CVFF force field (b) PCFF force field.

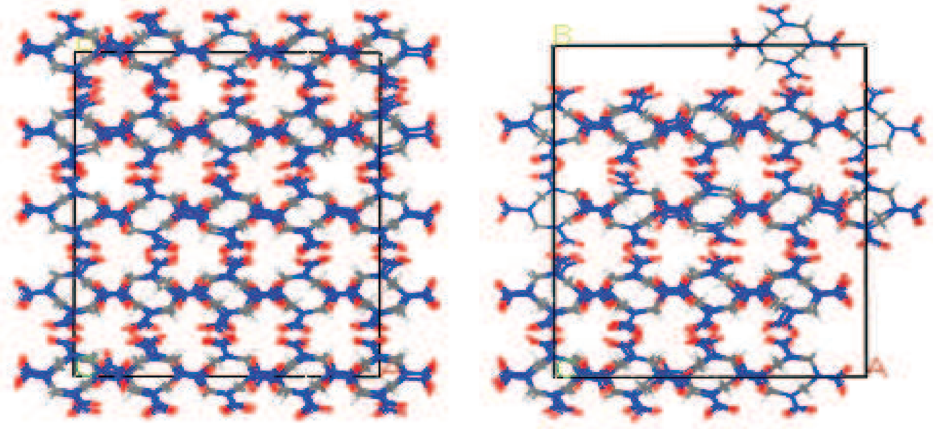


(a) Super cell (4×2×3) of $\beta$-HMX. (b) At 300 K and 0 GPa.



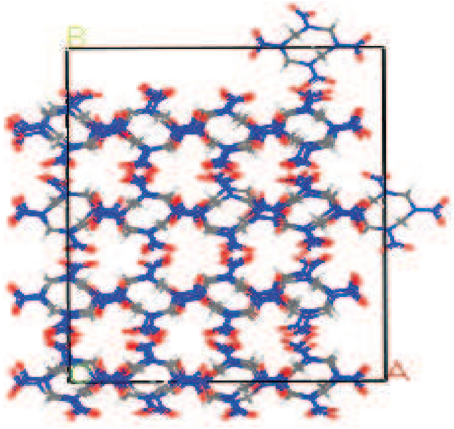
(c) At 370 K and 0 GPa.

(d) At 440 K and 0 GPa.



(e) At 300 K and 0 GPa.

(f) At 360 K and 0 GPa.



(g) At 430 K and 0 GPa.

Figure 4: The crystal structure of the super cell (4×2×3) of beta-HMX at differnt temperatures obtained with the CVFF force fiels (a)–(d) and the PCFF force field (e)–(g). The molecules are shown by stick representation where the red, blue and grey lines refer to oxygen, nitrogen and carbon, respectively.

## 4 Conclusions

In this paper, the cell volume, lattice constants and crystal structure properties of $\beta$-HMX are computed for a range of temperature and pressure using NPT-MD simulations. Unlike other recent simulations, we use the CVFF and PCFF force fields. However, our calculations overestimate $b$ and $c$ but underestimate $a$ and $\rho$ with the CVFF force field, overestimate $b$ but underestimate $a$, $c$ and $\rho$ with the PCFF force field. We observed that the cell volume exhibits sudden change at 370 K and 440 K with the CVFF force field, and at 360 K and 430 K with the PCFF force field, respectively. It indicates that phase transitions occurred at these temperatures which is in good accord with the experimental results.

**Acknowledgments.** This work is supported by grants from the National Natural Science Foundation of China under Grant Nos. 11174214 and 20773085, the State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology under Grant No. KFJJ09-02), the National Key Laboratory Fund for Shock Wave and Detonation Physics Research of the China Academy of Engineering Physics under Grant NO. 9140C671101110C6709, the Defence Industrial Technology Development Program of China under Grant No. B1520110002, and the National 973 Program under Grant Nos. 613143 and 2010CB731600.

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