

# Thermal Expansion of HMX

Jeffrey R. Deschamps · Mark Frisch ·  
Damon Parrish

Received: 15 October 2010 / Accepted: 3 February 2011 / Published online: 18 February 2011  
© Springer Science+Business Media, LLC (outside the USA) 2011

**Abstract** Thermal expansion of the  $\beta$ -phase of 1,3,5,7-tetranitro-1,3,5,7-tetrazocane ( $\beta$ -HMX,  $C_4H_8N_8O_8$ ) was studied in the temperature range of  $-150$  to  $30$  °C.  $\beta$ -HMX is monoclinic ( $a = 6.5255(10)$  Å,  $b = 11.0369(18)$  Å,  $c = 7.3640(12)$  Å, and  $\beta = 102.67(1)^\circ$ ), space group  $P2_1/n$ . On cooling from room temperature to  $-150$  °C the crystal under goes an anisotropic contraction with the  $a$ -axis virtually unchanged while the  $b$  and  $c$  axes contract by approximately 1.8 and 0.6% respectively. The disproportionate change in the  $a$  and  $c$  axes results in approximately a 0.4% change in the  $\beta$  angle. Despite the large differences in expansion along the different axes no phase change was observed.

**Keywords** 1,3,5,7-tetranitro-1,3,5,7-tetrazocane · HMX, anisotropic · Thermal expansion

## Introduction

1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (HMX, also known as cyclotetramethylene-tetranitramine, or tetrahexamine tetranitramine) is from a class of organic nitrate explosives known as nitramines. HMX was first synthesized in 1930 [10]. In explosives such as the nitramines higher density or larger molecules produce greater explosive yields. HMX is used almost exclusively in military applications, including as the detonator in nuclear weapons, in the form of polymer

bonded explosive, and as a solid rocket propellant. Additionally, the polymer bonded explosive compositions containing HMX are used in the manufacture of missile warheads and armor piercing shaped charges.

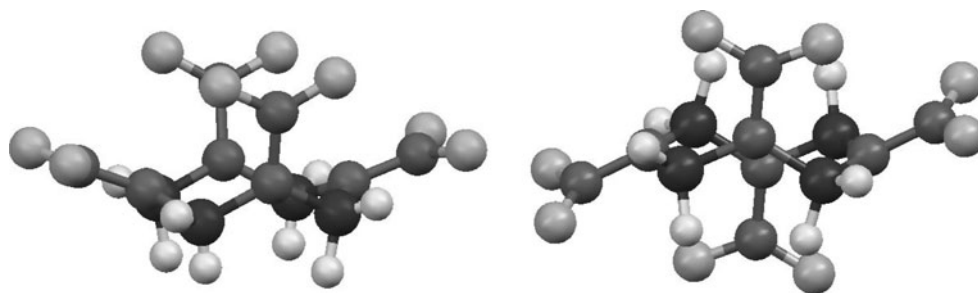
As noted previously, explosives with higher density tend to produce greater explosive yields. This characteristic of energetic materials which is proportional to density is known as detonation velocity. Detonation velocity is the velocity of the shock wave front traveling through a detonated explosive [3]. The force produced intensifies if the explosive is confined within a smaller area before detonation. This will yield a detonation velocity that is higher than if the explosion had occurred in open air. Thus, density is an important physical property of energetic materials such as HMX. Additionally, an increase in the density is also desirable because this will allow a larger mass of material to be packed into a limited volume of space.

One condition which can be adjusted to potentially alter the density is temperature. Thermal expansion is the tendency of a substance to adjust its volume in response to a temperature change. A crystal may expand along one or more of its axes as the temperature is lowered. This is referred to as negative thermal expansion. However, the more common form is known as positive thermal expansion which results in a contraction in at least one of the unit cell axes upon lowering of the temperature thus increasing the density of the material.

HMX is known to exist in four solid phase polymorphs ( $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ ) [4–7]. At room temperature, the  $\beta$ -HMX is the stable form. It has a monoclinic structure with  $P2_1/n$  (alternatively  $P2_1/c$ ) symmetry. The  $\alpha$ -HMX crystal structure is a higher temperature phase reported to be stable in the temperature range of  $103$ – $162$  °C. This phase is orthorhombic with  $Fdd2$  symmetry. The  $\delta$  polymorph occurs at even higher temperatures and is stable above

J. R. Deschamps (✉) · M. Frisch · D. Parrish  
Naval Research Laboratory, Code 6930, 4555 Overlook Avenue,  
Washington, DC 20375, USA  
e-mail: deschamps@nrl.navy.mil

**Fig. 1** The conformations of the  $\alpha$ -HMX (left, Cady et al. [4]) and  $\beta$ -HMX (right, Choi and Boutin [5]). The  $\delta$  and  $\gamma$  phases have conformations similar to the  $\alpha$ -polymorph



160 °C up to the melting point of approximately 280 °C. Crystals of the  $\delta$ -phase are hexagonal with space group  $P6_1$ . Hydrated HMX forms the meta-stable  $\gamma$ -phase for all temperatures at atmospheric pressure.

The conformations of the  $\alpha$ - and  $\beta$ -HMX molecules are quite different (Fig. 1). The  $\alpha$  form has twofold symmetry about an axis perpendicular to the ring plane through the center of the ring while the  $\beta$ -phase has a center of symmetry. The shape of the molecules in the  $\delta$  and  $\gamma$  phases is similar to the  $\alpha$ -polymorph with approximately twofold symmetry.

In this study, we investigate the thermal expansion of the  $\beta$ -phase of HMX by single crystal x-ray diffraction as the temperature is lowered to  $-150$  °C. The unit cell parameters were determined at a series of temperatures and the corresponding volumes and densities were calculated.

## Experimental Section

Single crystal X-ray diffraction data on HMX were collected using MoK $\alpha$  radiation and a Bruker APEX 2 CCD area detector. A  $0.286 \times 0.246 \times 0.136$  mm<sup>3</sup> crystal was prepared for data collection by coating with high viscosity microscope oil (Paratone-N, Hampton Research). The oil-coated crystal was mounted on a micro-mesh mount (Mitegen, Inc.) and transferred to the diffractometer. Data sets were collected at 123, 173, 198, 223, 248, 273, 293, and 303 K. To avoid crystal to crystal variability all data were collected on a single crystal. The crystal was monoclinic in space group  $P2_1/n$ . Corrections were applied for Lorentz, polarization, and absorption effects. The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$  values using the programs found in the SHELXTL suite (SHELXTL v6.10, 2000; [11, 12]. Parameters refined included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms on carbons were included using a riding model [coordinate shifts of C applied to H atoms] with C–H distance set at 0.96 Å. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre (deposition numbers 792927–792934). Copies of the data can be obtained, free of charge, on application to

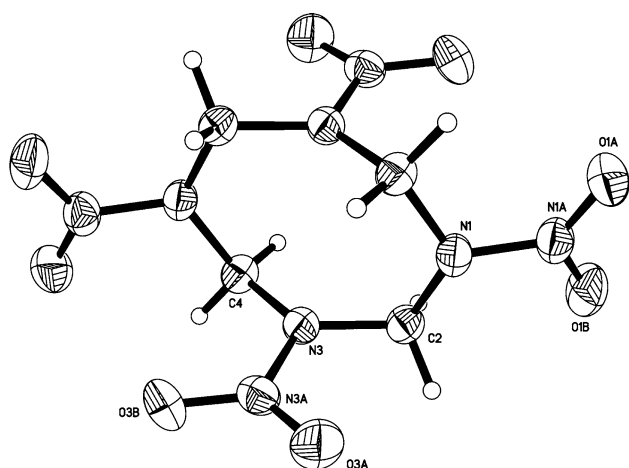
CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

## Results and Discussion

We have investigated the role of thermal effects on the structural parameters of the  $\beta$ -form of HMX. Complete data collection and refinement parameters for the x-ray study of HMX at 0 °C are given in Table 1 and depicted in Fig. 2. A full set of crystallographic parameters for all data

**Table 1** Crystal data and structure refinement for HMX at 0 °C

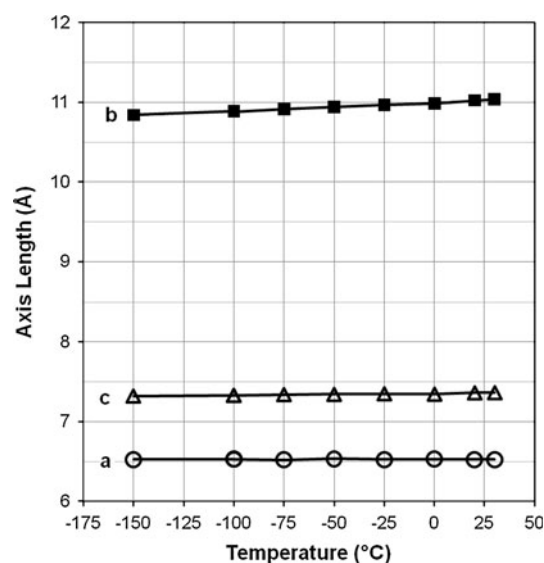
Empirical formula	C <sub>4</sub> H <sub>8</sub> N <sub>8</sub> O <sub>8</sub>	
Formula weight	296.18	
Temperature	273(2)°K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	$a = 6.5289(5)$ Å	$\alpha = 90^\circ$
	$b = 10.9875(9)$ Å	$\beta = 102.616(4)^\circ$
	$c = 7.3453(5)$ Å	$\gamma = 90^\circ$
Volume	514.20(7) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.913 mg/m <sup>3</sup>	
Absorption coefficient	0.182 mm <sup>-1</sup>	
$F(000)$	304	
Crystal size	$0.286 \times 0.246 \times 0.136$ mm <sup>3</sup>	
$\theta$ range for data collection	$3.39$ – $25.31^\circ$	
Index ranges	$-7 \leq h \leq 7$ , $-13 \leq k \leq 10$ , $-8 \leq l \leq 7$	
Reflections collected	2600	
Independent reflections	908 [ $R(\text{int}) = 0.0239$ ]	
Completeness to $\theta = 25.31^\circ$	97.2%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9691 and 0.9365	
Refinement method	Full-matrix least squares on $F^2$	
Data/restraints/parameters	908/3/97	
Goodness-of-fit on $F^2$	0.769	
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0331$ , $wR_2 = 0.1461$	
$R$ indices (all data)	$R_1 = 0.0341$ , $wR_2 = 0.1555$	
Largest diff. peak and hole	0.180 and $-0.270$ e Å <sup>-3</sup>	



**Fig. 2** The structure of  $\beta$ -HMX at 0 °C. Displacement ellipsoids are at the 50% level

(i.e. is available  $-150$  to  $30$  °C) is available in the deposited CIFs.

In order to determine the coefficients of thermal expansion (Eq. 1), measurements of the cell parameters were performed at temperatures in the range of  $-150$  to  $30$  °C (Table 2; Fig. 3). The largest observed change was in the  $b$ -axis which varies from  $11.0369$  to  $10.8400$  Å ( $1.78\%$ ) over the temperature range resulting in a thermal expansion coefficient of  $9.9 \times 10^{-5} \text{ K}^{-1}$ . A smaller change was observed in the  $c$ -axis ( $7.3640$ – $7.3207$  Å or



**Fig. 3** Thermal expansion of  $a$ ,  $b$ , and  $c$  axes in  $\beta$ -HMX (data from Table 2)

$0.59\%$ ) resulting is a thermal expansion coefficient of  $3.3 \times 10^{-5} \text{ K}^{-1}$ . The  $a$ -axis is nearly unchanged over the temperature range studies ( $6.5255$ – $6.5250$  Å or less that  $0.01\%$ ) with a thermal expansion coefficient of  $4.3 \times 10^{-7} \text{ K}^{-1}$ , however it should be noted that the correlation is poor as the slope is close to zero and the errors in determining the slope are of the same magnitude as the slope. This should be considered when viewing parameters

**Table 2** Experimentally determined unit cell and density of the  $\beta$ -form of HMX at different temperatures. ESD's are reported in parenthesis when available. Note that for earlier determinations of

HMX the reduced cell as reported in the Cambridge Structural Database [1] is used for comparison with the current data

Temp. (°C)	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	Density (mg/m <sup>3</sup> )	$\beta$	$N^a$	Source
30	6.5255(10)	11.0369(18)	7.3640(12)	517.45(14)	1.901	102.670(10)	689	1
20	6.5245(10)	11.0240(17)	7.3619(11)	516.68(14)	1.904	102.642(9)	700	1
0	6.5289(5)	10.9875(9)	7.3453(5)	514.20(7)	1.913	102.616(4)	1832	1
−25	6.5254(9)	10.9702(16)	7.3503(11)	513.53(13)	1.915	102.582(9)	730	1
−50	6.5334(9)	10.9419(14)	7.3421(10)	512.45(12)	1.919	102.491(2)	3940	1
−75	6.5206(9)	10.9123(16)	7.3395(11)	509.93(13)	1.929	102.467(9)	751	1
−100	6.5273(8)	10.8834(13)	7.3286(9)	508.54(11)	1.934	102.366(2)	4042	1
−100	6.5288(8)	10.8862(13)	7.3304(9)	508.91(11)	1.933	102.365(2)	4067	1
−150	6.5250(8)	10.8400(13)	7.3207(9)	505.97(11)	1.944	102.271(2)	4141	1
RT	6.533	11.032	7.351	516.88	1.903	102.68	nr <sup>b</sup>	2
RT	6.540	11.050	7.371	519.39	1.894	102.83	nr <sup>b</sup>	3
RT	6.540	11.050	7.371	519.39	1.894	102.83	nr <sup>b</sup>	4

<sup>a</sup> Number of reflections used in unit cell determination

<sup>b</sup> Not reported

<sup>1</sup> This study

<sup>2</sup> Zhitomirskaya et al. [15]

<sup>3</sup> Choi and Boutin [5]

<sup>4</sup> Cady et al. [4]

derived from the thermal expansion coefficient of  $a$ . Incorporation of errors in the unit cell determination into the determination of thermal expansion coefficients has a negligible effect on the coefficients for the  $b$  and  $c$  axes, the axes showing the largest change. Complete details for this analysis are available on request from the authors. The disproportionate change in the  $a$  and  $c$  axes results in change in the  $\beta$  angle which varies from  $102.670^\circ$  to  $102.271^\circ$  (approximately a 0.4%).

$$\alpha = (\Delta L/L_0) \Delta T^{-1} \quad (1)$$

Concomitant with the changes in unit cell dimensions are corresponding changes in cell volume ( $517.45$ – $505.97 \text{ \AA}^3$ , 2.22% change) and density ( $1.901$ – $1.944 \text{ mg/m}^3$ , 2.261% change).

The large difference between the expansion of the  $a$  and  $b$  axes results in an anisotropy of 230-fold. Despite this large anisotropy all measurements indicated that the crystal was the monoclinic  $\beta$ -phase of HMX in the entire temperature range studied.

There are no prior studies on the thermal expansion of HMX. Thermal expansion studies have been performed on TNT (Heberlein 1974; [14]. Macroscopic observations made on  $\alpha$ -TNT (Heberlein 1974) revealed a similar, although less pronounced, anisotropy with thermal expansion coefficients of  $3.8 \times 10^{-5}$ ,  $3.25 \times 10^{-5}$ , and  $7.55 \times 10^{-5}$  for the  $a$ ,  $b$ , and  $c$  axes respectively. In this study on  $\alpha$ -TNT the maximum anisotropy was about 2.3. Even with this small anisotropy an anomaly (i.e. second order phase change) was noticed in the observed expansion of all three axes at approximately 212 K but was not characterized by x-ray diffraction. The author speculates that this allowed relief of strain within the crystal resulting from the anisotropy. A later study on TNT [14] resulted in somewhat different thermal expansion coefficients ( $3.9 \times 10^{-5}$ ,  $4.9 \times 10^{-5}$ , and  $10.7 \times 10^{-5}$  respectively) with no indication of a phase transition in the range of 123–300°K. The maximum anisotropy in this later study was about 2.7. These results are also similar to those reported in a theoretical study where the expansion coefficients for TNT and PETN range from  $5.4\text{E-}05$  to  $3.5\text{E-}05$  (1.5-fold difference) and  $3.1\text{E-}05$  to  $2.1\text{E-}05$  (1.5-fold difference) respectively [13]. Both the experimental and theoretical results are in sharp contrast to the present study where the observed anisotropy between the  $a$  and  $b$ -axis was 230-fold. It should also be noted that there was no evidence of a phase change in the present study.

While the effect of temperature on density may be important in energetic materials of greater concern are the potential effects from anisotropic expansion. Anisotropic expansion can result in the formation of cracks in the crystals. These cracks have been shown to increase the sensitivity of energetic materials [2, 8, 9]. Thus

understanding the thermal expansion of an energetic material is an important step in developing insensitive munitions. In an x-ray study such as this with repeated cooling and warming crack formation would have been evident in spilt spots in the diffraction images, or in a more extreme case by the apparent formation of a twin. Since neither of these were observed we can only conclude that despite the large anisotropy observed in the thermal expansion there is no evidence for the formation of cracks in the crystals.

## Conclusions

The thermal expansion of  $\beta$ -HMX was studied measured from  $-150$  to  $30^\circ\text{C}$ . Thermal expansion coefficients derived from the unit cell parameters were  $4.3 \times 10^{-7} \text{ K}^{-1}$ ,  $9.9 \times 10^{-5} \text{ K}^{-1}$ , and  $3.3 \times 10^{-5} \text{ K}^{-1}$  for the  $a$ ,  $b$ , and  $c$  axes respectively.

Anisotropy in the expansion was observed and is greatest ( $\sim 230$ -fold) when comparing the  $a$  and  $b$  axes. This is approximately 100 times greater than the largest anisotropy observed in  $\alpha$ -TNT.

**Acknowledgments** This research was supported in part by the Office of Naval Research and the Naval Research Laboratory. The authors would like to thank Dr. Anthony Malanoski for his assistance in assessing how errors in the unit cell determination affect the calculated expansion coefficients. The views expressed herein are those of the authors and do not reflect those of the US Navy or the US Department of Defense.

## References

- Allen FH (2002) The Cambridge Structural Database: a quarter of a million crystal structures and rising. *Acta Crystallogr B* 58:380–388
- Bennett JG, Haberman KS, Johnson JN, Asay BW, Henson BF (1998) A constitutive model for the non-shock ignition and mechanical response of high explosives. *J Mech Phys Solids* 46(12):2303–2322
- Bolkhovitinov LG, Batsanov SS (2007) Theory of solid-state detonation. *Combust Explos Shock Waves* 43(2):219–221
- Cady HH, Larson AC, Cromer DT (1963) The Crystal structure of  $\alpha$ -HMX and a refinement of the structure of  $\beta$ -HMX. *Acta Crystallogr* 15(7):617–623
- Choi CS, Boutin HP (1970) A study of the crystal structure of  $\beta$ -cyclotetramethylene tetranitramide by neutron diffraction. *Acta Crystallogr B* 26(9):1235–1240
- Cobbedick RE, Small RWH (1974) The crystal structure of the  $\delta$ -form of 1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetraazacyclooctane ( $\delta$ -HMX). *Acta Crystallogr B* 30(8):1918–1922
- Main P (1985) Structure of the fourth form of 1, 3, 5, 7-tetranitro-1, 3, 5, 7-tetraazacyclooctane\* ( $\gamma$ -HMX), 2C4H8N8O8·5H2O. *Acta Crystallogr C* 41(9):1351–1354
- McGrane SD, Grieco A, Ramos KJ, Hooks DE, Moore DS (2009) Femtosecond micromachining of internal voids in high explosive crystals for studies of hot spot initiation. *J Appl Phys* 105(7):7

9. Ramaswamy AL, Shin H, Armstrong RW, Lee CH, Sharma J (1996) Nanosecond and picoseconds laser-induced cracking and ignition of single crystals of ammonium perchlorate. *J Mater Sci* 31(22):6035–6042
10. Schadler H, Lovelace A, Baskerville J, Capasso F, Firebaugh M, Gassner J, Jaffe M, Karasz F, Lipsitt HA, Meyyappan M, Peterson G, Phillips JM, Tressler R (2003) Materials research to meet 21st-century defense needs. The National Academies Press, Washington, D.C., p 255
11. Sheldrick GM (2008) A short history of SHELX. *Acta Crystallogr A* 64:112–122
12. SHELXTL v6.10 (2000) Bruker AXS Inc., Madison, WI
13. Sorescu DC, Rice BM, Thompson DL (1999) Molecular packing and molecular dynamics study of the transferability of a generalized nitramine intermolecular potential to non-nitramine crystals. *J Phys Chem* 103(8):989–998
14. Vrcelj RM, Sherwood JN, Kennedy AR, Gallagher HG, Gelbrich T (2003) Polymorphism in 2-4-6 trinitrotoluene. *Cryst Growth Des* 3(6):1027–1032
15. Zhitomirskaya NG, Eremenko LT, Golovina NI, Atovmyan LO (1987) Structural and electronic parameters of some cyclic nitramines. *Bulletin of the Academy of Sciences of the USSR Division of Chemical Science*. 36(3):525–529