Research paper

Synthesis, instrumental and explosive properties 1,1-diamino-2,2-dinitroethene (FOX-7)

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Abstract

In this work, FOX-7 ($C_2H_4N_4O_4$) has been successfully prepared in the laboratory scale through three main steps. Firstly by the preparation of the precursor 2-methylpyrimidine-4,6-diol ($C_5H_6N_2O_2$) which is also used in pharmaceutical applications in an economic method; the preparation was carried out by the preparation of sodium methoxide (CH_3ONa), the condensation reaction of acetamidine hydrochloride ($C_2H_7N_2Cl$) and diethyl malonate ($C_7H_{12}O_4$), filtration process, and finally acidifying step by concentrated hydrochloric acid. Secondly by nitration of the prepared 2-methylpyrimidine-4,6-diol ($C_5H_6N_2O_2$) with a mixed acid (HNO_3 / H_2SO_4). Finally by the hydrolysis step of the intermediate product 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione ($C_5H_2N_6O_{10}$) in distilled water. Instrumental characterization as Differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, scanning electron microscope (SEM) and elemental analysis were carried out to characterize the prepared 2-methylpyrimidine-4,6-diol and FOX-7. The results obtained approved the structures of the prepared 2-methylpyrimidine-4,6-diol and FOX-7. Explosive characterization as sensitivity test (to impact, friction, and heat), detonation velocity and brisance measurements were carried out to characterize the prepared FOX-7. It showed performance properties comparable to RDX, but it has lower sensitivity to impact and heat than RDX. Sensitivity to friction results showed no indication of initiation according to friction was noticed even when applying the maximum force (360 N) of the test apparatus. The performance results obtained showed detonation velocity and brisance more than RDX by 1.3 % and 0.3 % respectively.

Keywords: FOX-7, insensitive high energetic materials, 2-methylpyrimidine-4,6-diol, preparation, characterization

1. Introduction

The improvements of the high energetic materials technology incorporate the search for higher performance energetic materials with higher safety. The explosives progress has taken the direction to enhance the performance of explosives after the end of the First World War, and as a result, the sensitivity of explosives has been raised.

The request for the increase of safety in storage, handling, and transportation of the explosives has directed to the growth of insensitive munitions (IM). The design of these insensitive munitions (IM) reduces the probability of unwanted and unexpected explosion by external stimuli as shock, weapon fragments, and heat. This can be accomplished by modification of the explosive formulation, the external weapons system, or by both of them[1), 2)].

1,1-diamino-2,2-dinitroethene (FOX-7), was synthesized in 1998 by the Swedish defense research agency (FOI), emerged as a promising insensitive energetic material[3)]. Because of the high thermal stability of this substance, it gained extensive importance as a possible replacement for RDX; they found that the physical properties of FOX-7 are comparable with RDX, and the energetic properties of FOX-7 are slightly less than RDX[4)].

It is a new insensitive high explosive material with high thermal stability. It has a significant potential for application in insensitive munitions (IM)-compliant explosive compositions[5]. Researchers have current programs for the development and preparation of FOX-7 in pilot plant scale, in addition to the evaluation of its performance and explosive characteristics[6)–10)].

The main goal for this study was to prepare 2-methylpyrimidine-4,6-diol as a potential molecule which finds applications in pharmaceutical, explosives industries and used as a precursor for the preparation of FOX-7, then to prepare FOX-7 in laboratory scale in an economic method. For comparison purposes, RDX (1,3,5-Trinitro-1,3,5-triazinane) was also investigated. The instrumental characterization for 2-methylpyrimidine-4,6-diol and FOX-7 was investigated. The sensitivities to impact, friction and heat were determined. The brisance according to Kast method and the detonation velocity were measured.

2. Experimental method

2.1 Materials

The chemicals and the raw materials used in this study were of high purity; anhydrous methanol (CH_3OH, 99.8 %), ethanol (C_2H_5OH, 99.5 %), hydrocloric acid (HCl, 38 %), sulfuric acid (H_2SO_4, 98 %), nitric acid (HNO3, 68 %) were supplied by Beijing Chemical Works, China, sodium (Na, ≥ 99 %) was supplied by BePharm Ltd., Shanghai, China, acetamidine hydrochloride ($C_2H_7N_2Cl$, 99 %) was supplied by Qingdao Yao Ruifu Trading Co., China, diethyl malonate ($C_7H_{12}O_4$, 99 %) was supplied by Henan Tianfu Chemical Co., China, RDX ($C_3H_6O_6N_6$) was supplied by Hangzhou Dayangchem Co., China. A differential scanning calorimetry (DSC) (model STA 449 F5 Jupiter®) was used for the thermal stability characterization. A Fourier transform infrared (FTIR) spectroscopy (model NICOLET iN10MX) and a nuclear magnetic resonance spectroscopy (NMR) (model Bruker Ascend™ 500) were used for the spectroscopic analysis. A scanning electron microscope (SEM) (model Quanta™ FEG 250) was used to study the surface morphology. The weight percentage of the elements was determined by using Elemental analysis (model Flash 2000 elemental analyzer). The sensitivities to impact, friction, heat of FOX-7 and RDX were determined by using OZM ball fall hammer BFH-12A, OZM BAM friction test apparatus FSKM-10, OZM AET-402 automatic explosion temperature tester respectively according to standard test method[11)] . In order to determine the performance characteristics; the detonation velocity was measured by using Explomet-Fo®-2000 detonation velocity tester[12)], the brisance was determined by using OZM brisance Kast method according to standard test method[11)].

2.2 Experimental procedure

Many preliminary experimental trials were carried out to prepare 2-methylpyrimidine-4,6-diol (step 1) by the condensation reaction of acetamidine hydrochloride with diethyl malonate in the presence of sodium, ethanol and then acidified by concentrated hydrochloric acid. These preliminary experimental trails failed due to some notes encountered through the preparation trails as alcohol type, reflux time and temperature, filtration process, pH value adjustment and the low yield of the main products; it was necessary to improve the procedure of the preparation process.

Ethanol acts as reaction medium and it makes the process expensive, longer process time and the temperature are also contributed to the higher cost. So, the improvement of the preparation procedure focused on the development of an economic process concerned with alcohol type (anhydrous methanol instead of absolute ethanol), reflux time (4 hours instead of 6 hours) and temperature (65 °C instead of 90 °C).

Improvement of the preparation procedure of FOX-7 concerned with acid type (concentrated Nitric Acid 68 % instead of fuming Nitric Acid), filtration process (anti-acid filter paper, Buchner funnel, and vacuum pump are used).

2.2.1 Preparation of 2-methylpyrimidine-4,6-diol ($C_5H_6N_2O_2$)

Preparation process was carried out under reflux according to four main steps; firstly, by preparation of sodium methoxide (CH_3ONa), the condensation reaction of acetamidine hydrochloride ($C_2H_7N_2Cl$) and diethyl malonate ($C_7H_{12}O_4$), filtration process, and finally acidifying step by concentrated hydrochloric acid (HCl) as shown below:

1) In order to prepare sodium methoxide, a 1000 ml three-neck round-bottom flask equipped with water reflux condenser, dropping funnel, thermometer with lid and a magnetic stirrer bar in an ice cooling bath as shown in Figure 1 was charged with 250 ml of anhydrous methanol, then 9.4 g of sodium was added to the flask under stirring at a speed of 600 rpm until dissolution.

2) 16.4 g of acetamidine hydrochloride was added to the prepared sodium methoxide under stirring at 25 °C for 20 min. 25 ml of diethyl malonate was added to the reaction

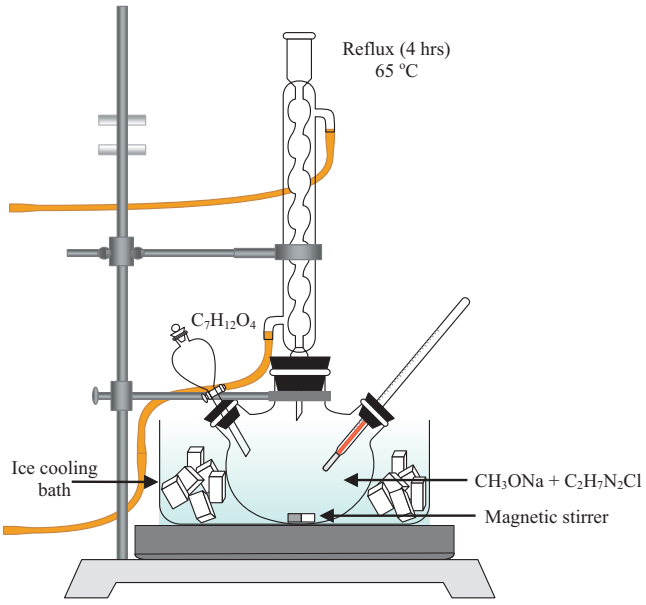

Figure 1 Experimental setup for preparation of 2-methylpyrimidine-4,6-diol.

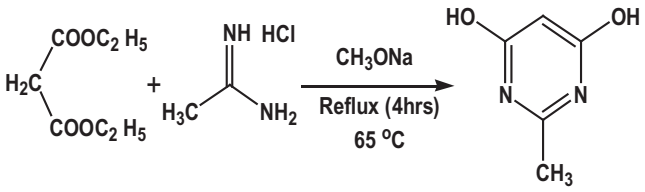

Figure 2 Synthetic outline of 2-methylpyrimidine-4,6-diol.

mixture, and the reaction mixure was continued stirring under reflux at 65 °C for 4 hrs. The synthetic outline from the condensation reaction is shown in Figure 2.

3) The resulting mixture which composed of sodium chloride and 2-methylpyrimidine-4,6-diol was cooled to 25 °C, and filtrated. The white filtrate was dissolved in 500 ml cold distilled water.

4) 15 ml of concentrated HCl was added to the solution to obtain pH 2. The content of the flask was subjected to a filtration process and the solid precipitate was washed with methanol and distilled water until an off-white crystalline material obtained. The water and methanol were then evaporated in a vacuum oven at 75 °C for 3 days to give 16.7 g of 2-methylpyrimidine-4,6-diol.

2.2.2 Preparation of 1,1-diamino-2,2-dinitroethene (FOX-7) ($C_2H_4N_4O_4$)

The preparation process of FOX-7 was carried out according to two main steps; firstly by nitration of the prepared 2-methylpyrimidine-4,6-diol ($C_5H_6N_2O_2$) with a mixed acid (HNO_3 / H_2SO_4), and then hydrolysis step of the intermediate product 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione ($C_5H_2N_6O_{10}$) in distilled water (H_2O) as shown below. The synthetic outline of FOX-7 is shown in Figure 3:

1) A 500 ml three-neck round-bottom flask equipped with dropping funnel, thermometer with lid and a mechanical stirrer in a water bath as shown in Figure 4 was charged with 63 ml of concentrated H_2SO_4, then 16.7 g of 2-methylpyrimidine-4,6-diol was added to the flask under vigorous stirring at a speed of 900 rpm until dissolution, the temperature was kept at 20 °C in the water bath during stirring. After cooling to below 8 °C, 26 ml of HNO_3 was slowly added dropwise to the reaction mixture over 30 min. The temperature was kept below 8 °C during the addition. After adding HNO_3, the reaction mixture was stirred for an additional 3 hours at 20 °C.

2) The reaction mixture was quenched by pouring it into cold ice distilled water (hydrolysis step) under vigorous stirring at a speed of 900 rpm, with the evolution of CO_2, the precipitate immediately dissolved in the distilled water. After a short time, canary-yellow solid crystals of 1,1-diamino-2,2-dinitroethene (FOX-7) precipitated. The content of the flask was subjected to a filtration process by using anti-acid filter paper, Buchner funnel ,and vacuum pump, then the solid precipitate washed by distilled water several times in order to remove the rest of the acid, and then dried in a vacuum oven at 50 °C for 10 days to give 15.9 g of 1,1-diamino-2,2-dinitroethene (FOX-7).

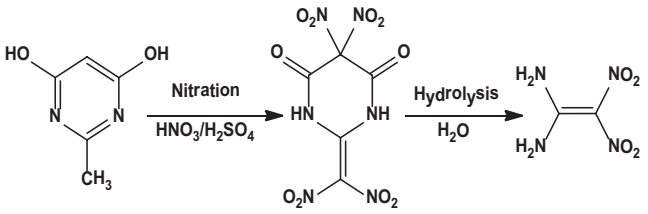

Figure 3 Synthetic outline of FOX-7.

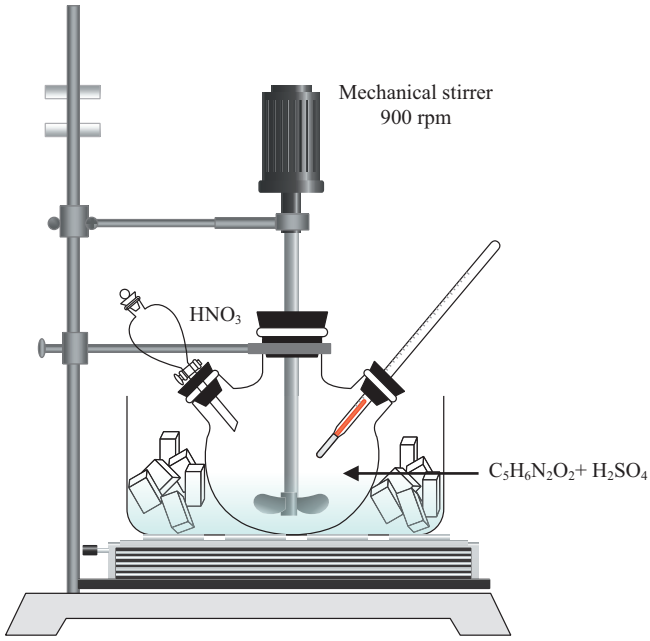

Figure 4 Experimental setup for preparation of FOX-7.

3. Results and discussion

In the following sections, results of experimental measurements and tests are presented and analyzed. Discussions are made and relevant findings singled out.

3.1 Results of instrumental characterization of 2-methylpyrimidine-4,6-diol and FOX-7

3.1.1 Results of differential scanning calorimetry (DSC) test

The thermal stability of the prepared 2-methylpyrimidine-4,6-diol and FOX-7 was studied using DSC technique. The onset endothermic and exothermic peak of each sample was determined at heating rate 10 °C. min^{-1}, the thermal behaviors of the prepared samples during the increase of temperature until their decomposition are presented in Figure 5 and Figure 6.

Figure 5 shows that there is only one endothermic peak at 375.45 °C, which approves the melting behavior of 2-methylpyrimidine-4,6-diol, correspond to the melting point reported at 376 °C[13].

Figure 6 shows that there is no melting point was noticed, there are two major exothermic peaks at 236.52 °C and 280.31 °C, which approves the thermal decomposition behavior of FOX-7, correspond to the decomposition behavior reported at 235 °C and 280 °C, respectively. Also showed two minor endothermic peaks at 111.68 °C and 166.3 °C, correspond to the ($\alpha \rightarrow \beta$) and the ($\beta \rightarrow \gamma$) polymorphic transitions reported at 112 °C and 165 °C, respectively[9].

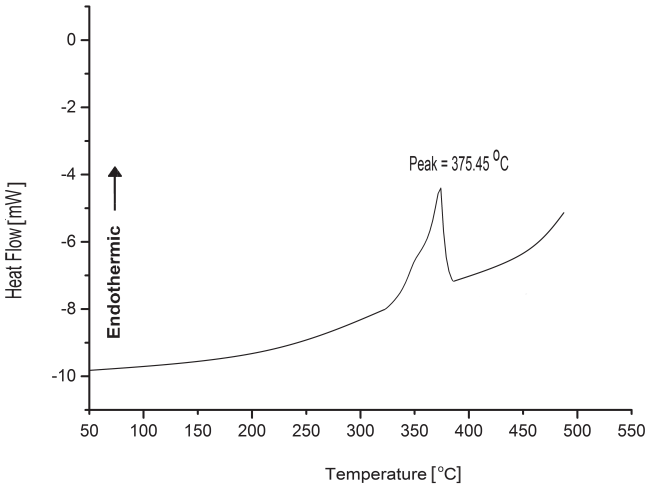

Figure 5 DSC spectrum of 2-methylpyrimidine-4,6-diol.

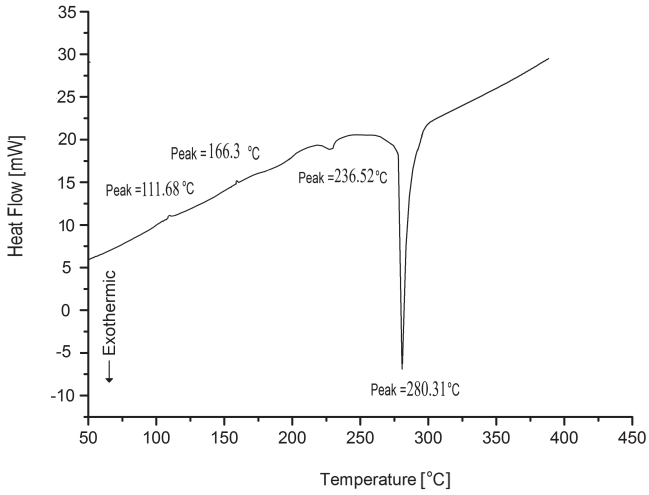

Figure 6 DSC spectrum of FOX-7.

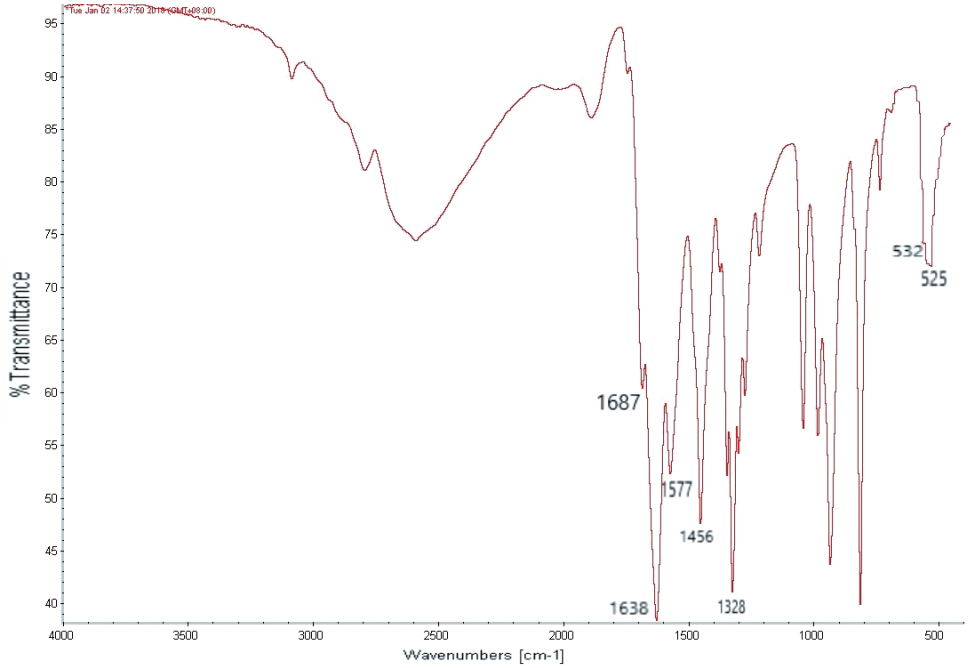

Figure 7 FTIR spectrum of 2-methylpyrimidine-4,6-diol.

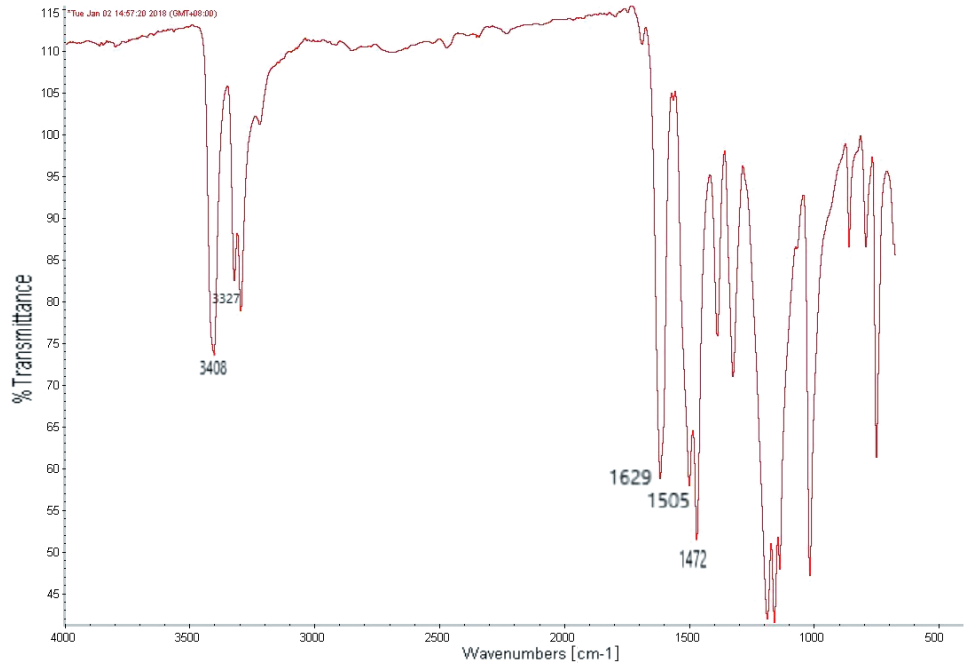

Figure 8 FTIR spectrum of FOX-7.

3.1.2 Results of Fourier transform infrared (FTIR) spectroscopy test

The FTIR spectrum was carried out to identify the functional groups of the prepared 2-methylpyrimidine-4,6-diol and FOX-7. FTIR spectrums of the prepared samples confirm the functional groups as presented in Figures 7 and 8.

The infrared spectrum of 2-methylpyrimidine-4,6-diol shows peaks at 525, 532, 1328, 1456, 1577, 1638, 1687 cm^{-1} as shown in Figure 7. This result coincides with the reference for the wave number of IR characteristics absorption peaks reported at 525, 533, 1329, 1456, 1577, 1641, 1687 cm^{-1} [13].

The infrared spectrum of FOX-7 shows peaks at 1472 (NO_2), 1505 (NO_2), 1629 (NH_2), 3327 (NH_2), 3408 (NH_2) cm^{-1} as shown in Figure 8.

This result coincides with the reference for the wave number of IR characteristics absorption peaks reported at 1472 (NO_2), 1520 (NO_2), 1636 (NH_2), 3330 (NH_2), 3408 (NH_2) cm^{-1} but with some shifts of peaks; this change may be related to the presence of possible impurities in the prepared FOX-7[13].

3.1.3 Results of nuclear magnetic resonance spectroscopy (NMR) test

The NMR spectrums of the prepared 2-methylpyrimidine-4,6-diol and FOX-7 were gained in DMSO-d_6 at 30 °C to identify the compound's unique

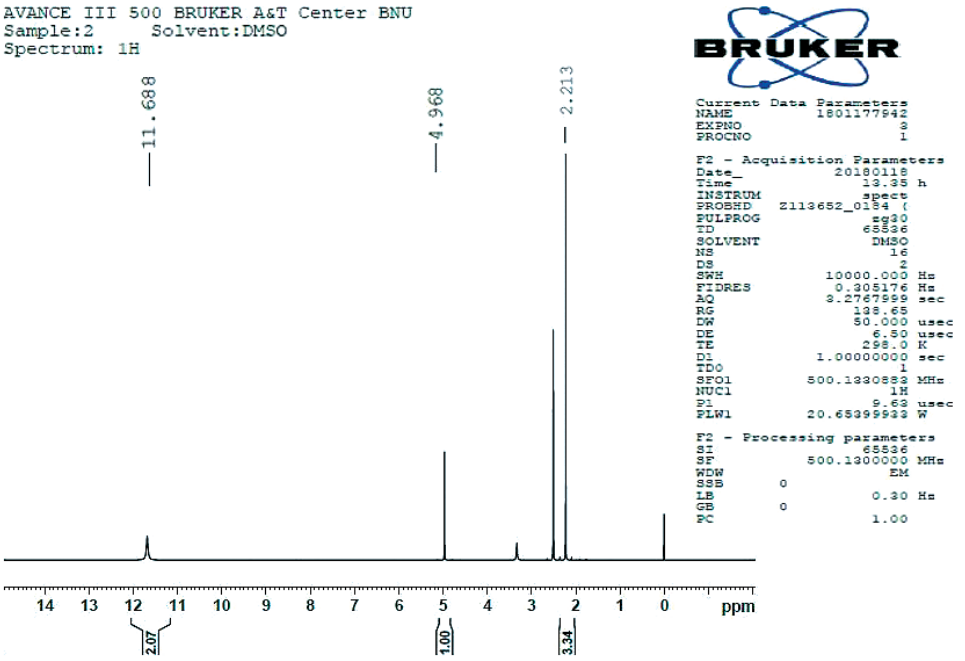

Figure 9 ^{1}H NMR spectrum of 2-methylpyrimidine-4,6-diol.

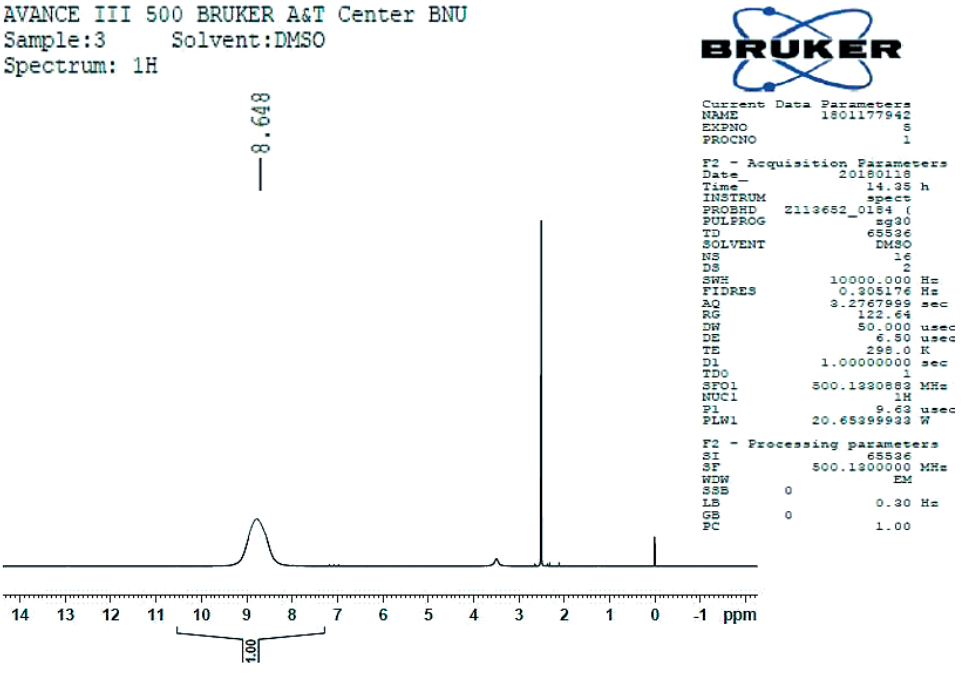

Figure10 ^{1}H NMR spectrum of of FOX-7.

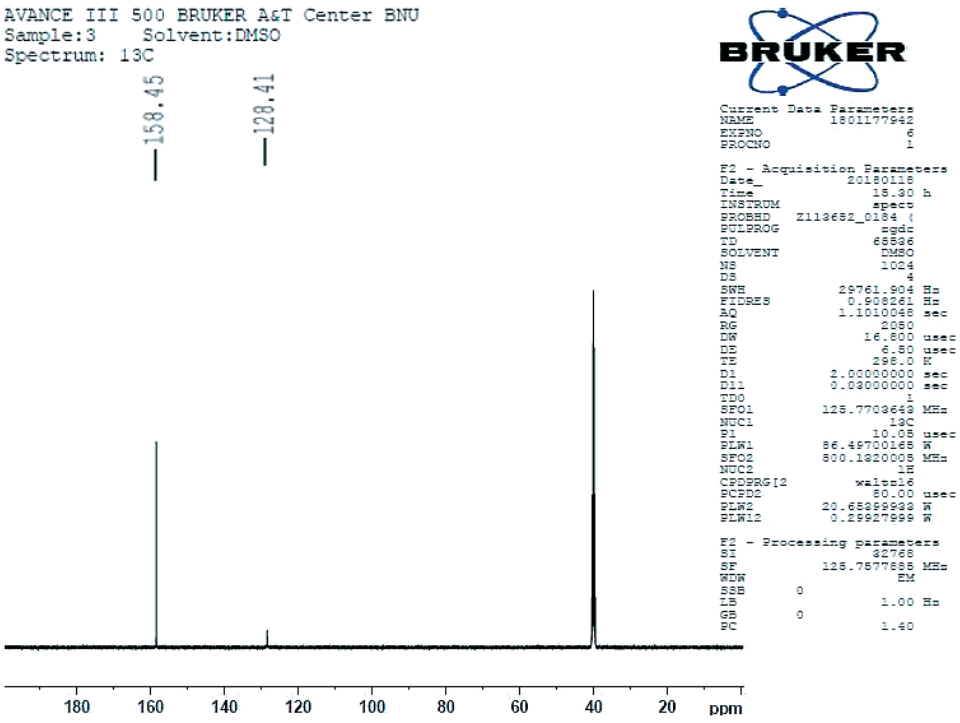

Figure11 ^{13}C NMR spectrum of of FOX-7.

structure. The ^{1}H and ^{13}C NMR spectroscopies of the prepared samples confirm the organic structure as presented in Figures 9 and 10.

The ^{1}H NMR spectrum of 2-methylpyrimidine-4,6-diol shows 3 peaks at δ 4.968 (s, 1H), δ 2.213 (s, 3H), δ 11.688 (s, 2 H) ppm as shown in Figure 11. This result coincides with the reference for the chemical shifts of the peaks reported at δ 4.95 (s, 1H) methyl, δ 2.21 (s, 3H) ppm and methylene groups[13].

3.1.4 Results of elemental analysis (EA) test

The elemental analysis was carried out to determine the empirical formula of the prepared 2-methylpyrimidine-4,6-diol and FOX-7.

The calculated and measured results of the elemental analysis (weight %) for 2-methylpyrimidine-4,6-diol ($C_5H_6N_2O_2$) and FOX-7 ($C_2H_4N_4O_4$) are shown in Table 1.

Table 1 The calculated and measured results of the elemental analysis for 2-methylpyrimidine-4,6-diol and FOX-7.

	2-methylpyrimidine-4,6-diol		FOX-7	
	Calculated	Measured	Calculated	Measured
C	47.61	47.32	16.22	16.18
H	4.79	4.49	2.72	2.62
N	22.21	22.74	37.83	37.69

3.1.5 Results of scanning electron microscope (SEM) test

The The SEM analysis was carried out to determine the surface morphology of the prepared 2-methylpyrimidine-4,6-diol and FOX-7 crystals as shown in Figures 12 and 13.

In the case of the prepared 2-methylpyrimidine-4,6-diol crystals which are presented in Figure 12, it is clear that the crystals have small size, and have a high degree of agglomeration. The surface of the crystals is smooth without cracks; also the shape of the crystal is near to hexagonal without sharp edges.

In the case of the prepared FOX-7 crystals which are presented in Figure 13, it is clear that the shape of the crystal is near to hexagonal-rod type. The surface of the crystals has cracks; this might be due to the presence of water inside the crystals and impurities. It has to be mentioned that the prepared FOX-7 crystals are technical grade without any crystal modification.

3.2 Results of explosive characteristics of FOX-7

The results of the explosive characteristics for FOX-7 were compared to the standard explosive RDX as shown in Table 2. For FOX-7; it is less sensitive to impact and heat comparing to RDX. The sensitivity to friction showed no indication even applying the maximum force (360 N) of the test apparatus. The performance results obtained showed values of its detonation velocity and brisance are larger than RDX by 1.3 % and 0.3 % respectively.

Table 2 Sensitivity and performance characteristics of FOX-7 and RDX.

	FOX-7	RDX
Sensitivity to impact [J]	24.7	7.5
Sensitivity to friction [N]	>360	120
Sensitivity to heat (ignition temp. [°C])	226	222
Detonation velocity [$m.s^{-1}$]	8864	8750
Brisance [kp]	1302	1298

4. Conclusions

In this paper, 2-methylpyrimidine-4,6-diol has been successfully prepared which is also used in pharmaceutical

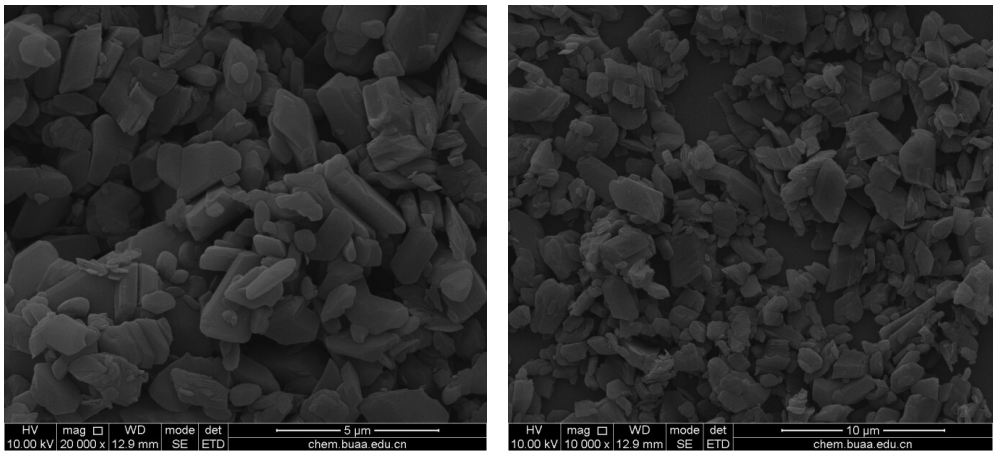

Figure12 SEM photos of 2-methylpyrimidine-4,6-diol crystals.

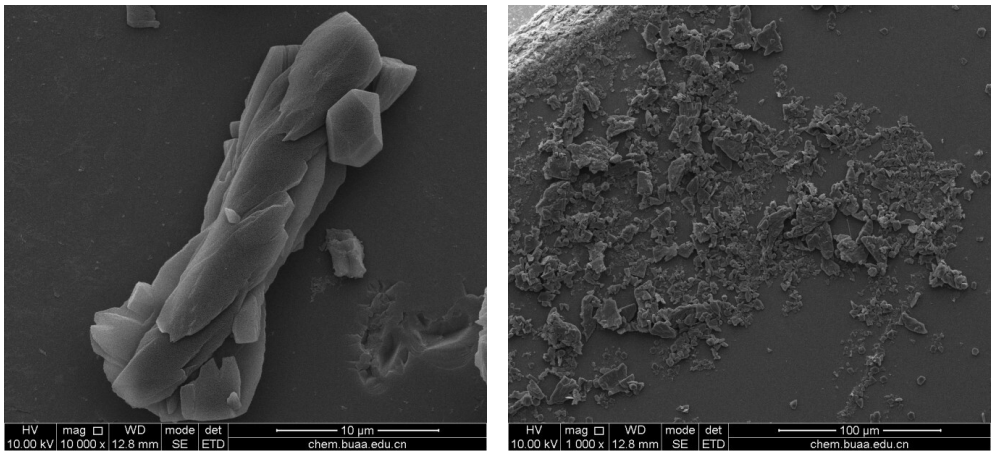

Figure13 SEM photos of FOX-7 crystals.

applications in an economic method. FOX-7 has been successfully prepared during this work using the prepared 2-methylpyrimidine-4,6-diol as a precursor. The preparation method is simple. A series of instrumental tests have been performed using thermal analysis (DSC), spectroscopic analysis (FTIR and NMR), surface morphology study (SEM) and elemental analysis to evaluate the prepared products. Sensitivities (to impact, friction and heat) tests and performance tests (detonation velocity and brisance) were applied in order to evaluate the explosive characterstics of FOX-7 in comparison with RDX. The results of this work are in agreement with the results reported at the other researches. FOX-7 showed performance properties comparable to RDX, but it has lower sensitivity to mechanical stimuli.

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