A Novel Approach for Synthesis of Low Sensitive FOX-7 with a high % yield

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Abstract: Attaining a high performance is one of the most seeking demands in the energetic materials field. However, achieving that goal while keeping a high level of safety became a serious puzzle. 1,1-diamino-2,2-dinitroethene (FOX-7) could be a promising candidate to solve that issue regarding its favorable explosive characteristics together with its low vulnerability. However, its high cost and low yield obtained via the FOI method limit its use in the field of insensitive munition (IM). In this work, we propose a novel approach to synthesis the FOX-7 crystals with high purity, a relatively high yield, and an extremely low impact, friction, ignition sensitivities. The obtained crystals were characterized using FTIR Spectroscopy, Proton NMR Spectroscopy, IKA impact test apparatus, BAM friction test apparatus, Chilworth deflagration test apparatus, and the adiabatic calorific bomb. Results confirmed the successful preparation of pure FOX-7 crystals with a promising yield of 64%, in comparison to the yield of the FOI method of 55%, and extremely low sensitivities using our proposed approach.

Keywords: Energetic Materials, FOX-7, Insensitive Munitions (IMs), Low-vulnerable, PBXs.

1. Introduction
Many research projects are focused on improving the performance characteristics of energetic materials while maintaining low sensitivity. The progressive deployment of Insensitive Munitions (IM) by numerous defense forces throughout the world is compatible with these objectives. These systems dependably meet their performance, readiness, and operational requirements on-demand, but their violent response to unexpectedly dangerous stimuli is kept to a manageable level [1]. Being dropped [2,3],[4],[5], shell impact [6,7], and detonation by influence are some of the risks that IM is meant to address.

IM-compliant explosive compositions can be created using one of two methods. For example, a Polymer Bonded Explosive (PBX) can be created by combining novel binders like GAP with energetic components already found in flexible polymeric matrices known as binders (glycidyl azide polymer). TATB, NTO, ADN, HNIW, and CL20 are all examples of inherently low-sensitive energetic compounds that can be used to make explosives [9–19]. TATB, NTO, ADN, HNIW, and CL20 are all examples of intrinsically low-sensitive energetic components that can be used to make explosives.

For the time being, the commercial availability of FOX-7 is limited because of its expensive cost. Although it performs in the same ballpark as RDX, the FOX-7 is far less sensitive. When compared to cyclotrimethylene trinitramine (RDX), FOX-7’s first findings from the Swedish inventors revealed that it was much less responsive to diverse forms of danger stimuli and somewhat higher in performance. Its processing capabilities and compatibility with other materials are as yet unknown. Future research will undoubtedly focus on these traits.

Table 1 compares some of the FOX-7’s characteristics to those of RDX. FOX-7’s theoretically expected great performance has yet to be shown empirically. FOX-7 has the potential to make a significant contribution to the advancement of non-lethal weapons. This combination might be a new hope in the realm of explosives. It was launched by FOI colleagues in the fall of 1998.
An important part of this study is examining how FOX-7 is synthesized and characterized in contemporary low-sensitive explosive formulations and how it functions as an energetic material in those formulations. DSTO's Explosives Group [20] is reporting on current and prospective research that employs thermochemical calculations to analyze several PBXs based on FOX-7, which might be used to replace the standard Comp B. [20].

Table 1. Properties of FOX-7 in comparison with RDX.

| Property                        | FOX-7  | RDX  |
|---------------------------------|--------|------|
| Density, (ρ), (g/cm$^3$)        | 1.885  | 1.816|
| Detonation velocity, (D), (m/sec$^2$) | 8870   | 8750 |
| Detonation pressure, (P), (GPa) | 34     | 34.6 |
| Oxygen balance, (O$_b$)         | -21.6  | -21.6|
| Activation energy, (kcal/mole)  | 58     | 40   |
| Heat of formation, (ΔH), (kcal/mole) | -32    | 16   |
| Impact sensitivity, (Nm)        | 15-25  | 7.5  |
| Friction sensitivity, (N)       | >340   | 120  |
| Ignition temperature, (ºC)      | 226    | 223  |

2. Experimental Work

2.1 Chemicals
Methanol (HPLC grade) was purchased from Sigma-Aldrich (Steinheim, Germany) and then was exploited as a solvent without any further purification. Sodium Methoxide, Acetamidine Hydrochloride, and Diethyl Oxalate were acquired from Al-Gomhoria company for medicines and medical supplies (Cairo, Egypt). Hydrochloric Acid (37%), Sulphuric Acid (95%), and Nitric Acid were obtained from Harshit Export (Mumbai, India).

2.2 Preparation of 1,1-Diamino-2,2-dinitroethene (FOX-7) according to the modified (FOI) method
The heterocyclic starting material 2-methoxy-2-methylimidazolinedione was synthesized by condensing diethyl oxalate with acetamidine hydrochloride at high dilution in methanolic sodium methoxide and then recrystallizing it from the methanol. First, 2-methoxy-2-methyl-5-imidazolidinedione was nitrated, resulting in 2,2-dinitomethylene-5-imidazolidinone, which was hydrolyzed to yield FOX-7.

2.2.1 Preparation of 2-methoxy-2-methyl-4,5-imidazolidinedione. The magnetic stirrer bar, drying tube, and dropping funnel were all included in the 2L round bottom flask. At an initial concentration of 0.9455g/cm$^3$, the flask was filled to its full capacity with methanol (430ml) and sodium methoxide (30% in methanol, 112ml). At room temperature, 18.24 g of acetamidine hydrochloride was added to the agitated solution to produce a suspension. Thereafter, the mixture was stirred for an additional hour with the addition of 27.94 grams of diethyl ethyl oxalate in methanol (200 milliliters). Using strong hydrochloric acid at a temperature below 30 ºC, the reaction was brought down to a pH of around 4. Filtration through filter aid (APS 1739) removed the insoluble salts, and the filtrate was evaporated to dryness at a temperature of 30 ºC to yield a white solid. Filtration of 160 ml boiling methanol was done to remove the insoluble salts from this material. The filtrate was then diluted to a
final volume of 160 ml. In the morning, the crystallized white substance was collected and dried after cooling overnight in the refrigerator (17.75 g, 64 percent).

2.2.2 Nitration of 2-methoxy-2-methyl-4,5-imidazolidinedione to prepare 2,2-Dinitromethylene-4,5-imidazolidinedione. In an ice bath, 198 ml of concentrated sulphuric acid was added to a 500 ml round bottom flask equipped with a magnetic stirrer, thermometer, dropping funnel, and drying tube. The cooled acid solution was gently diluted with 2-methoxy-2-methyl-4,5-imidazolidinedione (35.4 g), resulting in a bright yellow solution. It took 60 minutes for the color of the combination to change from yellow to deep red, and finally to an orange suspension with the addition of 70 percent nitric acid (43 ml). For 30 minutes, the suspension was swirled at room temperature. It was then air-dried and filtered before being utilized in the following process.

2.2.3 Hydrolysis of 2,2-dinitomethylene-4,5-imidazolidinedione to produce FOX-7. This reaction was carried out in a 500 ml conical flask, with the addition of the crude 2,2-dinitromethylene-4,5-imidazolidinedione to the water (120 ml). In order to keep the temperature stable between 20 and 30 degrees Celsius, 30 percent ammonia in water was supplied to the suspension at a rate that kept the temperature between 20 and 30 degrees Celsius. After 2 hours of stirring at room temperature, the resulting suspension was filtered and the solid product was recovered using filtering and water washing (4 times). The brilliant yellow crystalline material was identified as 1,1-diamino-2,2-dinitroethene after air and vacuum drying at 60 °C and 7 mmHg (19.66 g of yield percentage about 54.1 percent).

2.2.4 Recrystallization of obtained FOX-7 crystals. Recrystallization of FOX-7 crystals was performed utilizing a DMSO ionic solvent as a co-solvent system (20:80 w/w). The crystallization process took place at 60 °C, where the remaining crystals were dissolved in methanol then collected via filtration. A non-agitated cooling was used to accelerate the FOX-7 crystal's growth. The resulting crystals were subjected to different characterization processes to confirm their identity, purity, shape, and quality of the final percentage yield of FOX-7 crystals.

3. Characterization

3.1 Melting Point Determination
A simple technique was used in measuring the melting point of 2-methoxy-2-methyl-4,5-imidazolidinedione. A small amount of a sample was inserted in a capillary tube which was placed into a special metallic block with a glass window and calibrated thermometer. The metallic block was heated over a hot plate. The melting temperature of the sample was carefully observed via the glass window. Three consecutive trials for each sample were performed and the average values were determined.

3.2 FTIR Spectroscopy
Jasco FTIR -6200 was used to identify the product through the FTIR spectrum. If the sample is solid, the solid sample and KBr would be ground, mixed, and pressed in the form of a disc having standard dimensions. The wavenumber range used was 500-4000 cm⁻¹ which is the appropriate range for most organic compounds. Using the FTIR spectrum made it possible to identify the main functional groups of the prepared materials.

3.3 Proton NMR Spectroscopy
Varian NMR 300 MHz spectrometer is the most powerful tool available for organic structure determination was used to study the nuclei of 1H and 13C. The examined sample was dissolved in a suitable solvent (DMSO) then the sample was measured due to the magnetic field generated from the spinning charged nucleus.

3.4 Determination of Explosive Characteristics of FOX-7

3.4.1 Sensitivity Tests
3.4.1.1 Determination of sensitivity to impact. The upper limit of sensitivity to impact [24] was determined using IKA apparatus which consists mainly of a falling steel hammer (2 or 5 kg) moving on vertical rails provided with a calibrated scale. The testing piston part consists of 2 steel cylinders and a casing. Weighed samples of about 0.01 g of the explosive are spread over the central surface of the bottom cylinder, and then the piston is located in its position. The impact of the weight, through the piston, transferred to the sample may or may not result in its
initiation according to the sensitivity of the sample; sound, light, or smoke are usually observed. If none of these effects are observed, initiation failure is reported. The test results were reported as a relation between the percentage of initiations and the drop height having constant mass.

The experiment was performed using a weight of 2 or 5 kg and drop height was increased gradually. For each height, six consecutive trials were performed and the corresponding percentage of initiation was recorded. The upper sensitivity limit, \( H_{100} \) was used to identify the minimum height at which 100% initiation was achieved. Similarly, the lower sensitivity limit, \( H_0 \), was used to identify the maximum drop height at which no initiation was achieved. The impact energy for dropping weight at each height is calculated according to the equation:

\[
E_i = m \times H \times g
\]

Where:
- \( E_i \) is the impact energy (J).
- \( m \) is the mass of the falling hammer (kg).
- \( H \) is the drop height (m).
- \( g \) is the acceleration due to gravity (9.8 m/sec\(^2\)).

3.4.1.2 Determination of sensitivity to friction. Chilworth BAM friction test apparatus, (UK) was used to determine the sensitivity to friction [24]. The apparatus consists of a hard unglazed porcelain plate of dimensions 25x25x5 mm, fixed in a movable table sliding at constant speed between two marks by an electric motor. A cylinder is fixed on a clamping holder. An apparatus lever can be loaded with different loads at ten different positions. The value of the force, measured in Newton, for a certain load and certain position was obtained from the calibration table. The table is shifted to the starting position after each trial by turning the rotor of the electric motor; sensitivity to friction is determined by spreading about 0.01g of the dry explosive on the surface of the porcelain plate in the form of a thin layer. Different loads are used to change the normal force between the porcelain pistil and the plate; force varies from nearly 5 to 320 N. The sample initiation may be observed through sound effects, smoke appearance, or by the characteristic smell of the decomposition products. Six consecutive trials were performed for each load and lever position.

3.4.1.3 Determination of ignition temperature. The ignition temperature can be experimentally determined by heating at a constant rate, an explosive sample of a given mass until the ignition occurs [24]. The ignition temperature test was performed by using the Chilworth deflagration test apparatus, made in the UK. It consists of an aluminum block comprising three vertical holes to accommodate test tubes, a programmable heating controller in a separated control box allowing remotely controlled temperature, a heat sink, and an electric fan to accelerate the cooling down of the heating block.

Three samples of 0.2 g each were dried up and ground to suitable particle size then inserted into 3 test tubes which were placed vertically into the heating block and the temperature was uniformly increased at the rate of (5°C/min) until deflagration of the sample occurs. The ignition temperature was monitored digitally on the control unit and the average temperature for the three samples was calculated.

3.4.1.4 Determination of ignition temperature at constant delay period of ignition (5 sec). Delay of ignition of an explosive at a certain temperature was experimentally determined by placing an explosive sample of a fixed mass at that temperature which should be higher than the previously determined ignition temperature of the explosive. The test is done using the same apparatus as before. The temperature was adjusted and fixed until the ignition took place and delay time was recorded. The samples of 0.05 g each were inserted into three test tubes already heated in the aluminum block to the investigated temperature and a stopwatch was used to measure the time elapsed till ignition. The test was repeated at different temperatures till the obtained delay period was exactly 5±0.1 sec.

3.4.1.5 Determination of heat of the explosion. The measurement of the explosion heat is analogous to the determination of the heat exchange in various chemical or physical processes. The experiment is performed in an adiabatic calorimeter assembly [24] and is based on the observation of the temperature increase in the calorimetric vessel during the combustion process. The heat capacity of the calorimeter assembly is determined by a calibration
procedure during which a substance of known explosion heat is used. Consequently, the explosion heat of the sample under test is determined by a similar run, using the relation:

\[ Q = K_w \times \Delta T \]

Where:
- \( K_w \) : Heat capacity of the calorimeter (units)
- \( \Delta T \) : Temperature difference of the vessel (units)

The adiabatic calorimeter assembly consists of a calorimetric bomb, a calorimetric vessel filled with water, a stirrer, and a thermometer.

4. Results and discussion

Crystals obtained after applying the modified synthesis approach followed by a recrystallization process were found to have an interestingly high yield of \( \sim 64\% \). The melting point of 2-methoxy-2-methyl-4,5-imidazolidinedione (step I) was found at 158.2 °C, which coincides with that of FOI [25]. However, the melting point of FOX-7 could not be measured due to the near value of deflagration point (218 °C) from the point of FOX-7 decomposition. FTIR spectrum, as shown in Figures 1 and 2 and listed in Table 2, confirmed the successful preparation of FOX-7 through this technique. Table 2 describes how much the Characteristic peaks coincide with the standard FOI results. The NMR spectrum of 2-methoxy-2-methyl-4,5 imidazolidinedione according to experimental results is the same as the FOI results but with some shifts of peaks due to the presence of impurities in main product; Figure 3 for \(^1\)H and Figure 4 for \(^{13}\)C. The NMR spectrum of 1,1-diamino-2,2- dinitroethene (FOX-7) according to experimental results is the same as the FOI results but with some shifts in peaks due to the traces of impurities found in the main product.

The results developed for the sensitivity values, as given in Table 4, against the impact and friction stimuli were found to be \( (12-25) \) J and \( (>320) \) N respectively. The ignition temperature of the obtained FOX-7 was 223 °C. These results coincide with the standard sensitivity values given by FOI [26][27]. The activation energy of the obtained FOX-7 was found to be 55 kcal/mol, which is very close to that of FOI [28]. The heat of explosion of the obtained FOX-7 crystals was 4091kJ/kg 4079 kJ/kg which is acceptable in comparison to the standard FOI value, 4091 kJ/kg [26]. These results confirm the successful synthesis of pure FOX-7 crystals through the proposed novel technique.

![Figure 1. The FTIR characterization of 2-methoxy-2-methyl-4,5 imidazolidinediones (step 1).](image)
Table 2. The FTIR characterization of 2 methoxy-2-methyl-4,5 imidazolidinediones and 1,1-diamino-2,2-dinitroethene (FOX-7)

| FTIR spectroscopy |   |   |
|-------------------|---|---|
| 2 methoxy-2-methyl-4,5 imidazolidinediones (step I) |   |   |
| Function group    | FOI Results | Experimental Results |
|                   | Wave number (cm$^{-1}$) | Wave number (cm$^{-1}$) |
| NH                | 3249 | 3270 |
|                   | 1755 | 1755 |
|                   | 1477 | 1477 |
|                   | 1427 | 1405 |
|                   | 1388 | 1388 |
|                   | 1179 | 1260 |
|                   | 1124 | 1101 |
|                   | 1047 | 1028 |
|                   | 790  | 790  |
|                   | 729  | 700  |
|                   | 674  | 680  |
|                   | 597  | 601  |
| C=O               | 1636 | 1654 |
| NO$_2$            | 1520 | 1532 |
| NO$_2$            | 1472 | 1440 |

1,1-diamino-2,2-dinitroethene (FOX-7)

| Function group | FOI Results | Experimental Results |
|----------------|-------------|----------------------|
|                | Wave number (cm$^{-1}$) | Wave number (cm$^{-1}$) |
| NH$_2$         | 3408         | 3400                 |
|                | 3330         | 3260                 |
|                | 1636         | 1654                 |
| NO$_2$         | 1520         | 1532                 |
| NO$_2$         | 1472         | 1440                 |
Table 3. NMR characterization of 2 methoxy-2-methyl-4,5 imidazolidinedione and 1,1-diamino-2,2-dinitroethene (FOX-7)

| Type of atom | FOI Results | Experimental Results |
|--------------|-------------|----------------------|
| $^1$H        | chemical shift (δ) | chemical shift (δ) |
| $^3$H, CH$_3$| 1.58        | 1.571                |
| $^3$H, OCH$_3$| 2.98       | 2.972                |
| $^2$H, NH    | 9.92        | 9.96                 |
| $^{13}$C     | chemical shift (δ) | chemical shift (δ) |
| $^{13}$C     | 26.86       | 27.8                 |
|              | 47.86       | 47.88                |
|              | 91.59       | 100.7                |
|              | 159.84      | 168.96               |

Figure 2. The FTIR characterization of 1,1-Diamino-2,2-dinitroethene [FOX-7] (step 3).
Figure 3. The $^1$H NMR characterization of 2-methoxy-2-methyl-4,5 imidazolidinedione (step 1)
Figure 4. The $^{13}$C NMR of 2 methoxy-2-methyl-4,5 imidazolidinediones (step 1).
Figure 5. The $^1$H NMR of 1,1-Diamino-2,2-dinitroethene (step 3)

Figure 6. The $^{13}$C NMR of 1,1-Diamino-2,2-dinitroethene (step 3).
Table 4. Explosive sensitivity test results of FOX-7.

| Explosive properties | FOI       | Experimental |
|----------------------|-----------|--------------|
| Impact sensitivity, (J) | 15-25    | 12-25        |
| Friction sensitivity, (N) | >340     | >320         |
| Ignition temperature, (°C) | 226      | 223          |
| Activation energy, (kcal/mole) | 58       | 55           |

5. Conclusions

1,1-Diamino-2,2-dinitroethene (FOX-7) has been successfully prepared with lower sensitivity and higher performance in comparison to RDX. Interestingly, the % yield of the obtained FOX-7 crystals via our modified approach [64%], was higher than that of the standard method of the Swedish Defense Research Agency (FOI) [58%]. The proposed novel technique involved several modifications; adjusting the reaction stoichiometry at which the exact amount instead of excess amount of sodium methoxide (17.207 g) was used according to the stoichiometric reaction equation, adjusting of the pH value to approximately 9 instead of 4 by the addition of concentrated hydrochloric acid to improve the precipitation and separation of white crystals of NaCl, starting the reaction procedure by reducing the reaction temperature lower than 10 °C instead of 30 °C which reduce the formation of byproducts, and finally, the filtrate was evaporated to dryness by using rotary evaporator instead of vacuum oven to achieve a complete drying at < 30°C to avoid thermal decomposition of step I product through long drying time of vacuum oven. The FTIR spectrum and the NMR spectrum of 2-methoxy-2-methyl-4,5 imidazolidinedione (step I) and 1,1-diamino-2,2- dinitroethene (FOX-7) were the same as the FOI standard results. The sensitivity results were near to that of FOI results and lower than that of RDX. The heat of explosion of FOX-7 was measured as 4079 kJ/kg while it was calculated as 4091 kJ/kg according to FOI results.

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