5-Nitro-1,2,4-triazole-3-one：A Review of Recent Advances

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Abstract：The 3-Nitro-1,2,4-triazole-5-one（NTO）is a high energy density materials of keen interest for both commercial and scientific worlds owing to its reduced sensitivity，better thermal stability and high performances. It plays a significant role to replace the current energetic ingredients. In this review，we summarize various strategies involved in the synthesis of NTO as well as the existing approaches to tailor its particle morphology and sizes. The most prominent properties of NTO，such as insensitivity and performance，which are usually required to produce efficient formulations，have been concisely discussed. In addition，this overview reports on some newer forms of NTO including derivatives and co-crystals available in the literature，which can enhance the NTO features and extend its applications. The advantages and shortcomings of various NTO forms for specific and potential use are also highlighted together with the attempts made to overcome these issues. Therefore，efforts will certainly continue to improve characteristics and performances of NTO either by chemical modification or by co-crystallization in order to produce promising formulations for widespread applications in the near future.

Key words：Triazolone；3-nitro-1,2,4-triazole-5-one（NTO）；synthesis；properties；particle morphology；derivatives；co-crystals；applications

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1 Introduction

The study of high energetic materials，*e.g.*，explosives，propellants，and pyrotechnics，has drawn much attention in military and civilian engineering science. The most commonly used energetic materials（EMs）are 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane（HMX），1,3,5-trinitro-1,3,5-triazacyclohexane（RDX），2,4,6-trinitrotoluene（TNT），ammonium perchlorate（AP），nitroglycerin（NG），and nitrocellulose（NC）[1−4]. Recently，some of new energetic materials have shown prominent applications，

such as hexaazahexanitroisowurtzitane（HNIW，CL-20），2,6-diamino-3,5-dinitropyrazine-1-oxide（LLM-105），1,1-diamino-2,2-dinitroethylene（FOX-7），1,3,3-trinitroazetidine（TNAZ），2,4,6-triamino-1,3,5-trinitrobenzene（TATB）and 3-nitro-1,2,4-triazole-5-one（NTO）[5−8].

The synthesis，modification and application of such materials are still very active. Major effort sare devoted to develop high performance EMs with not only excellent combustion / detonation properties，high densities，and positive oxygen balances，but also good thermal stabilities，insensitivities to external forces，inexpensive synthesis，safe handling and good environmental compatibility，among others. However，achieving a fine balance between the various requirements of physicochemical properties is an interesting but challenging task because enhancement in some properties（*e. g.* performance）often comes at the expense of the others（*e. g.* molecular stability）.

NTO has captured a major role in research of

EMsas one of the important insensitive high explosive. A key characteristic of the thermally stable NTO is its insensitivity to impact, friction, heat, spark and shock waves[9]. It is relatively easy to synthesize. It displays performance characteristics comparable to those of the currently commonly employed secondary explosives and possesses an appropriate potential to be used as an explosive and propellant ingredient[10]. This compound has been shown to be less harmful to human health than traditional explosives[11]. It can be also pressed without a binder into desired morphology having a high density[12]. Several authors have tailored its particle size and morphology in order to meet the requirement of energetic materials formulations. Spherical morphology is revealed to be appropriate for better processability and has great impact on scale to alter the performance and insensitivity towards a sudden mechanical stimuli than non-spherical crystals[13-14].

However, this nitrogen heterocyclic energetic compound presents some drawbacks, what limit its further applications, such as negative oxygen balance, negative enthalpy of formation and acidity. To overcome such shortcomings, the researchers have adopted two main approaches. The first one concerns the preparation of NTO derivatives owing to its acidity and the second one is dedicated to the formation of NTO-co-crystals. The first approach is the famous one, where several metal and amine salts, and other derivatives of NTO have been produced and other continue to appear. Several of the latter compounds exhibit interesting physicochemical properties. The second new approach, which is the co-crystallization, may provide a promising pathway to use NTO. A co-crystal is a type of a molecule, displaying intermolecular interaction arising from hydrogen bonds, π-stacking, *van der Waals* forces, and halogen bonds. It is reported that co-crystallization can tailor the crystal density of EMs without changing their chemical structure. Besides, the insensitivity may be decreased without sacrificing the performance[15]. Various NTO co-crystals have been recently investigated theoretically and

experimentally. It is shown that this methodology provides an opportunity to modify the physicochemical properties and prepare superior co-crystals with better-integrated properties at amolecular level[16].

Several review papers and book chapters have been published in the last two decades dealing with NTO, its derivatives as well as the conventional synthesis procedures and applications[5,14,17-21]. However, the focus of the current article is different from the published literature and where appropriate, specific points covered in published literature are summarized and/or referenced out to the corresponding paper/book/patent. One of the prime objectives of this review is to summarize and emphasize the up-to-date procedures used to produce NTO showing their advantages and drawbacks.We believe that it may provide a strong base for the future development in this emerging area of research. An overview of the NTO particle morphology and size control will be provided as well as their effects on the physicochemical properties. The recent NTO derivatives and the different NTO-based co-crystalsas potential substances, that could replace the current energetic ingredients, are discussed. Current applications of NTO in energetic formulations are also highlighted.

2 Synthesis of NTO

Manchot and Nolle are considered as the pioneers in the synthesis of NTO, although their structure assignment was wrong, by using a two-step process[22]. The first step is dedicated to the production of triazolone, which undergone the nitration process in the second step. Chipen et al. and other scientists have followed this approach few decades later[23-26]. Slight modifications on the synthesis procedure have been performed by Lee et al. at Los Alamos National Laboratory, USA, and published the first report on the explosive nature of NTO during 1980s[27]. The recognition of such energetic features has promoted its extensive theoretical studies, synthesis and characterization[19, 28]. Various synthesis methods have been explored worldwide for preparing this energet-

ic compound，where the focus is the development and improvement of the synthesis pathways of such heterocyclic compound. The detailed methodologies of the efficient synthesis methods are given bellow.

## 2.1　Synthesis of Triazolone (TO)

Both of the two isomers 1，2，4-triazol-5-one and 1，2，4-triazol-3-one are abbreviated as triazolone or oxytriazole. It is considered as an intermediate product. Triazolone is a heterocyclic compound containing three nitrogen atoms，one $C=N$ double bond and carbonyl group. It can be prepared by different ways as depicted in Fig.1.
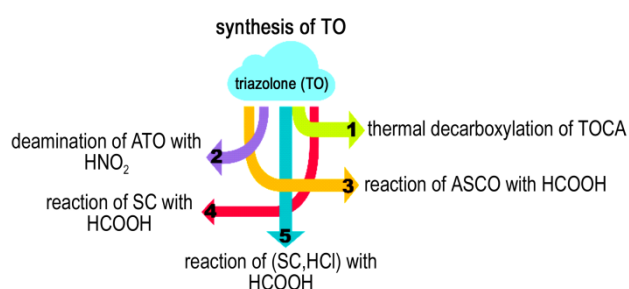
Fig.1　Different methods to synthesize triazolone. TO：1，2，4-triazole-5-one；SC：semicarbazide；ASCO：acetone semicarbazone；ATO：4-amino-1，2，4-triazol-5-one；TOCA：3-carboxylic acid-1,2,4-triazol-5-one

The thermal decarboxylation of 1，2，4-triazol-3-one carboxylic acid is used by Manchot et al. to synthesis triazolone[29-30]. The obtained yield was low. Few years later，Chipen et al. have tried to enhance the yield of such reaction by improving the yield of 1,2,4-triazol-3-one carboxylic acid（Ⅲ）using different concentrations of sulfuric acid（15%，25% and 35%）to decompose the 3-diazo-1,2,4-triazole-5-carboxylic acid（Ⅱ）to generate the compound Ⅲ[29]. This latter was decarboxylated at 205-210 ℃ to produce 75% of TO. The reaction process is displayed in Scheme 1. The similar authors have synthesized TO by acylation of acetone semicarbazone with formic acid，the intermediate reaction has produced diformylsemicarbazide，which on prolonged heating generates TO. The authors mentioned that the reaction yield does not exceed 10%.

In another work，Kröger et al. have prepared TO by the deamination of 4-amino-1，2，4-tri-
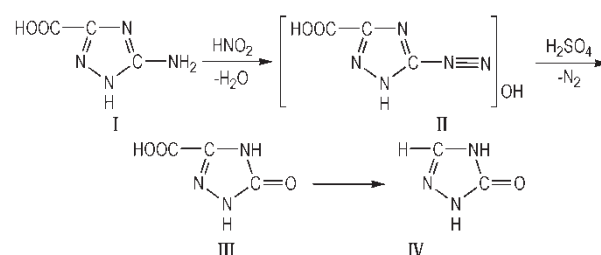
Scheme 1　TO synthesis from the thermal decarboxylation of 1，2，4-triazol-3-one carboxylic acid[29]

azol-5-one with nitrous acid[26]. During 1990s，Becawe et al. have boiled either semicarbazide alone or semicarbazide hydrochloride with formic acid（90%）[5,31-32]. They revealed that the best way to get a better yield（70%）and greatest purity（99%）is to use either a solid semicarbazide hydrochloride（SC）itself or by forming SC in situ employing semicarbazide and aqueous hydrochloric acid. This method based on solid SC remains the most and widely employed method to produce TO[9,12,33-35].

2.2　Nitration of TO

A number of research works dealing with thenitration of TO have been undertaken by several scientists. The synthesis of NTO was achieved using one of the following nitrating agents：fuming nitric acid[22]，nitric acid at different concentrations[5,27,36] or sulfuric-nitric acid mixture[37]. Many synthesis strategies were adopted to improve both reaction process and yield（Table 1）. This process can be performed in one or two-steps.

Table 1　Yield of NTO production using different nitrating agents

| nitrating agent	yield/%	reference
fuming nitric acid（98%）	–	[22]
fuming nitric acid/water	67	[29]
fuming nitric acid（with initial cooling）	70-75	[25]
nitric acid（70%）（one pot reaction）	75	[38]
nitric acid（70%）（two-step reaction）	80	[21]
nitric acid/sulfuric acid（one pot）	77	[38]
nitric acid/sulfuric acid/heating with microwave	74	[34]
cyclodextrinnitrate ester/sulfuric acid/water	88	[12]
metal nitrate/sulfuric acid	80	[39]

2.2.1　Nitration of TO with Nitric Acid

NTO can be obtained by nitration of triazolone

（TO）in diluted / concentrated nitric acid or simply by using fuming nitric acid, which may be prepared by adding excess nitrogen dioxide to nitric acid. Broadly, the synthesis procedure is not an easy process, because several parameters can affect the chemical reaction such as the concentration of the acid, its purity, the ratio, the duration and temperature of the reaction, to name a few. During 1980s, various synthesis routes have been developed. Spears et al. have made a concise review dealing with the preparation methods of NTO, where they pointed out the employment of different ratios of semicarbazide, formic acid, nitric acid alone or mixed with sulfuric acid under different experimental conditions[38]. They have reported that the yield of NTO varied between 36% – 75%. Many research works have been devoted to enhance the yield of NTO by studying the nitration of TO using different concentration of nitric acid(65% to 100%)[22-24,26-27,31,40].

In 1993, Becawe and Delcos[31] optimized the nitration process previously introduced by Manchot and Noll[22]. They investigated various parameters such as the nitration temperature, the nitration ratio （HNO$_3$/triazolone）, reaction time, and dilution ratio. They deduced that the nitration ratio of 5 is an acceptable promise, the temperature values between 20 ℃ and 30 ℃ are perfectly acceptable, the reaction time of three hours provides a maximum yield, and the dilution ratio of slightly less than unity seems to be optimum. However, they pointed out that the dissolution of TO in nitric acid should be started at a temperature close to 0 ℃ because it is highly exothermic before allowing the reaction medium to reach the room temperature. The process was done in two steps as given bellow（Scheme 2）. Mukundan et al. have also used the same two-step process, where they synthesized TO followed by NTO after nitration using HNO$_3$[41]. They reported a yield of 80% after crystallization from water. Singh et al. employed the similar synthesis route by using 70% nitric acid for nitration of TO to NTO[42].

Zbarsky and Yudin performed a detailed investigation of the nitration kinetics of TO in 70%–100%
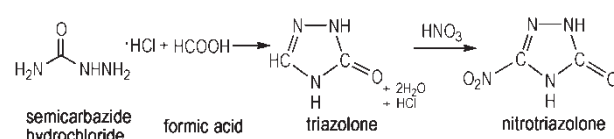
Scheme 2 NTO synthesis from semicarbazide hydrochloride[31]

nitric acid, and they found that the process can be simulated by pseudo-first-order[43]. They reported that the yield of NTO did not depend on temperature in the range of 0–30 ℃. The reaction time, which decreases by the increase of temperature, was independent on both the initial acid concentration in the range of 90%–98% HNO$_3$ and the ratio of HNO$_3$ to triazolone in the range of 4–8 mol HNO$_3$ per mole TO. Nevertheless, at acid concentration exceeding 77%, 1-nitro-1,2,4-triazol-one is obtained within the first minutes of the nitration. It was found that a total destruction of the TO ring occurred with the formation of N$_x$O$_y$, CH$_2$O and CO as decomposition products when H_0>1; whereas, if H_0<−1, de-nitration reaction occurred with the formation of TO. The similar authors demonstrated that NTO is produced from N—NTO via hydrolysis process, where TO is an intermediate, rather than via a rearrangement[20]. The mechanism of formation and disappearance of N—NTO is shown in（Scheme 3）[33]. Furthermore, it was revealed that the yield of NTO significantly decreased, when more concentrated nitric acid 96%–100% is employed[43]. This behavior is due to the fast generation of N—NTO during the nitration of TO rather that the formation of NTO. Consequently, it is recommended to avoid the formation of the low stable N—NTO during the production of NTO.
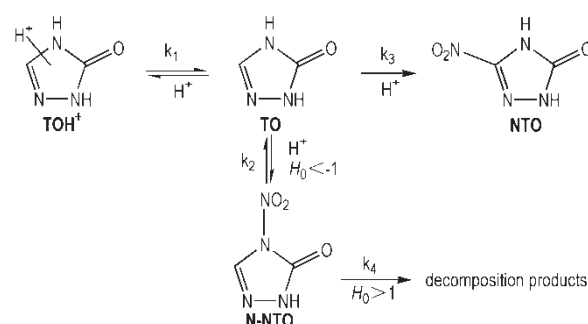
Scheme 3 Mechanism of the nitration of TO with a high concentrated nitric acid[33]

Recently，Zhao et al. have investigated the influence of concentration of reactants（HNO₃ and TO）and reaction temperature on the rate of synthesis of NTO by using an experimental kinetic model[44]. They established an exponential kinetic model，that can suitably predict the rate of NTO synthesis from TO. It was also confirmed that the concentration of HNO₃ had an obvious effecton the reaction rate.

2.2.2 Nitration of TO with Sulfuric-nitric Acid Mixture

The mixture of concentrated nitric acid and sulfuric acid，known as sulfonitric mixture，has been employed successfully for more than 17 decades in industrial nitration processes. The main role of sulfuric acid is to turn nitric acid into kinetically significant species，the nitronium ion，NO_2^+[45].

Spears et al. have tried to find the optimum of both temperature and duration of the of nitration reaction[38]. They followed a one-pot nitration procedure，what means that TO，as an intermediate，was not separated from the system but nitrated directly. The nitration process is occurred by using concentrate sulfuric-nitric acids at different temperatures. They claimed an optimum yield of 75.3% at 65 ℃ for 2 h. They have deduced that the decrease of HNO₃ volume or temperature，or the decrease of reaction time decreased the yield of the reaction. In another work，Li described the one-pot synthesis procedure of NTO. In this process，a cyclocondensation of semicarbazide with formic acid is occurred，and followed by nitration to get a yield of 76.8%[46].

Smith and Cliff[21] followed the similar procedure adopted by Spears et al.，given above to produce NTO. In their one-pot synthesis route，the mixture of formic acid and SC is done at ambient temperature. The reaction takes place at a very desirable temperature of 65 ℃ and the authors get a yield of 80%.

Kim et al.[37] described another route to prepare NTO. It consists of mixing triazolone with a mixture of 98% sulfuric acid and 70% nitric acid in a reactor at 25 ℃，then raising the temperature to around 40 ℃ in order to generate a crystal nucleus of 3-nitro-1，2，4-triazol-5-one. Finally，the reaction was completed by heating the reaction mixture to 65 ℃. Recently，Zeckeru et al. produced NTO using a two-step process[47]. A sulfuric acid：nitric acid mixture was drop wise added to TO under stirring at room temperature. Then，the temperature of the reaction was increased to 72−75 ℃ and maintained for 6 h. They obtained a yield of 73%. In another research work，Lasota et al. have produced NTO by nitration TO with a mixture containing HNO₃/H₂SO₄/H₂O at a temperature of 55−65 ℃[14]. The obtained product was recrystallized by water and its decomposition temperature was 267 ℃.

The nitration of TO using the sulfonitric system at a temperature of 65 ℃（Scheme 4）is currently considered as one of the efficient procedures to synthesize NTO and with satisfactory yields as it is widely employed by several authors [14,17,19,33,47−48].
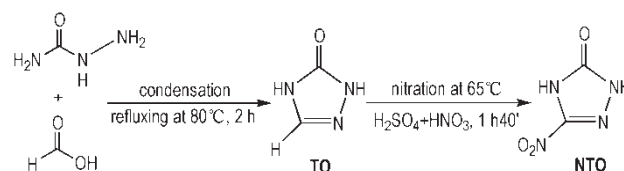
Scheme 4 Synthesis of NTO procedure using sulfonitric mixture[14,17,19,33,47−48]

2.2.3 Microwave Assisted-synthesis of NTO

The synthesis of EMs usually required heating steps. This later can be done by using oil baths and heating jackets. These techniques are slow，less safe，energy consuming and can lead to overheating and decomposition of products. Microwave（MW）irradiation seems to be an efficient substitute to conventional heating methods，since it uses the ability of liquids or solids to transform electromagnetic energy into heat energy. The emergence of microwave energy as an eco-friendly procedure provides several discrete advantageous over conventional synthetic methods，such as higher yields，reproducibility，safe operation，controllable heating，energy economy，better reliability，low cost，fast reaction，directly selective，and decreased environmental pollution[49]. In the recent few years，microwave assisted

chemical synthesis has attracted considerable attention of the scientific community. It is employed in several fields such as catalysis[50−51], sensors[52], pharmaceutical[53], food[54], nanomaterials and polymer synthesis[55−59], among others. However, this method is rarely employed in the field of synthesis of EMs and not much information are available[34,56−57,60−62].

Saikia et al. have reported the synthesis of NTO using microwave-assisted method. They employed a 70% nitric acid/sulfuric acid mixture（15 ℃）as nitrating media. The reaction was performed in a microwave reactor equipped with a condenser and exposed to MV radiation（201 W）for 10 min at 65 ℃. The quality of the synthesized product was confirmed by spectroscopic techniques[34]. The authors demonstrated that using MV radiation as a heating source the reaction time was drastically decreased along with similar reaction yield of the final product with respect to the conventional methods. It is reported that the rate of reaction of nitration of triazolone is enhanced. Furthermore, it is worthy to note that the amount of NO_x throughout the reaction period is far less than that evolved in the case of conventional heating process, owing to the short duration time required. This is a prominent benefit in terms of gaseous hazardous materials mitigation.

2.2.4 Cyclodextrin Nitrate Ester/H_2SO_4 System to Synthesis NTO

Cyclodextrines（CD）are natural cyclic oligosaccharides, obtained during bacterial digestion of cellulose. These CD can be constituted by six（α-CD）, seven（β-CD）, and eight（γ-CD）glucopyranoside units[63]. The nitration of CD generates EMs, cyclodextrin nitrate esters（CDNs）. The latter compounds, solid in nature, have exhibited good thermal stability, safe to handle, and acceptable solubility in organic solvents, what makes them synthetically more useful. CDN has been already tested as ingredient of gun propellants or explosive composites, and it was demonstrated that such formulations present greater energy, higher thermal stability, and lower sensitivity to impact in comparison to nitrocellulose-based composites[64]. Recently, Deshmukh and

al. have explored for the first time β-CD nitrate ester（CDN）as nitrating agent to synthesize NTO[12]. The authors optimized the synthesis parameters by examining the reaction that involves TO, sulfuric acid and water, in addition to CDN. They demonstrated that the nitronium ion species were generated by employing CDN and sulfuric acid. The synthesis procedure is depicted in Scheme 5.
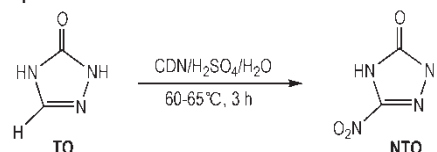
Scheme 5 Synthesis of NTO procedure using Cyclodextrin Nitrate Ester[12]

The characterization of the obtained NTO showed the efficiency of such synthesis method. A higher yield（88%）along with better quality hasbeen exhibited. Furthermore, it has been demonstrated that the manipulation of solid CND offers different benefits such as safer handling and less hazardous strategy compared to the use of liquid concentrated nitric acid.

2.2.5 Nitration of TO by Using Metal Nitrate

Due to environmental issues caused by acid waste generated by the conventional method of nitration in the synthesis of NTO, Saikia et al. proposed another alternative nitration process[39]. It involves the substitution of nitric acid by other safe and environmentally friendly nitrate components. The authors employed different inorganic nitrates such as potassium nitrate（KNO_3）, sodium nitrate $NaNO_3$ and silver nitrate（$AgNO_3$）with H_2SO_4 as mild nitrating agents to assess the selectivity and the yield of TO nitration. It has been revealed that the NTO obtained by using metal nitrate/sulfuric acid as nitrating agent have comparable properties to that obtained by the conventional method. Furthermore, it was shownthat $AgNO_3$ had better reactivity compared to theother two, and provided ahigher yield（about 80%）.

2.3 Heat Effects During the Nitration Process of TO

It has been established that during the nitration

process of TO in different concentrations of nitric acid，a variety of heat effects can influence the synthesis process[5,44]. A better understanding of such heat effects can insure the safety of the NTO production，even in large-scale manufacturing. Few years ago，Trzciński et al.[33] have studied the heat and kinetics of reaction in calorimetric measurements，and modeling the phenomena occurring in a nitration reaction during NTO synthesis，in order to understand the phenomena accompanying the nitration of TO and provide data to well describe the process. They determined the average heat of reaction employing different mixtures of $HNO_3/H_2SO_4/H_2O$. The authors deduced that the total heat of TO nitration consisted of thermal effects of dissolution and nitration of TO. More recently，Zhao et al. have investigated the heat effect of TO nitration by HNO_3 using different kind of calorimeters[9]. They demonstrated the existence of five kinds of thermal effects：the heat of process of dosing TO（$\Delta H_{TO,dosing}$），the heat of dissolution TO（$\Delta H_{TO,dissolution}$），the heat of reaction（$\Delta H_r$），the heat of crystallization of NTO（$\Delta H_{NTO,crystallization}$）and finally the heat caused by change in concentration of HNO_3（ΔH_{HNO_3}）. They pointed out that the main contribution to the total exothermic effect during the NTO synthesis came from the heat of reaction in different concentration of HNO_3. They reported also that the contribution ability rank of other four thermal effect is different，depending on the concentration of nitric acid.

3   Properties of NTO

The determination and understanding of the properties of EMs is a key factor to develop new formulations with better stability，higher performance，reliability，safety and low toxicity. Their measurement and estimation can allow an accurate screening of potential energetic candidates. Owing to its interesting properties，NTO has attracted significant attention over the world. It presents several desirable features，viz. high heat of formation，high density and high oxygen balance that are crucial parameters
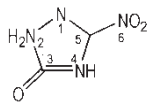
for increasing the performance of an energetic material. Broadly，a number of recent reviewsand research works have described，in a critical and comprehensive way，the relevant contributions carried out on the characterization of NTO. Ma et al. have discussed various properties of NTO such as crystal structure，thermal behaviors，toxicity，and various NTO derivatives[65]. Several prominent features such as the physicochemical properties（density，crystallinity，morphology，thermal and spectroscopic properties），sensitivity，thermodynamic properties（heat capacity，entropy，solubility），decomposition kinetics，degradation，destruction，and detonation characteristicsare also reported[10,17,19,21,35,42,66−68]. Therefore，only some important details are presentedbelow to avoid duplication.

3.1   General Features

Some physicochemical and spectroscopic properties of NTO are displayed in Table 2. NTO presents favorable oxygen balance and high density compared to the conventional explosives. Furthermore，owing to its better physicochemical properties combined with a higher energy release on decomposition and better stability，NTO is considered as a vital energetic molecule to substitute the common explosives，which are currently less attractive because of issues associated with catastrophic mishaps，sympathetic detonations as well as dimensional instability at higher temperatures[17−18, 41].

Fig. 2 shows some sensitivity characteristics of NTO compared to conventional EMs[17,19,21]. It can be seen that NTO has low sensitiveness to friction compared to PETN，RDX，and HMX and similar to TNT and TATB. Moreover，NTO is less sensitive to shock compared to PETN，RDX，and HMX and slightly more sensitive than TATB. Considered as the workhorse of explosives since it determines the storage and handling of the materials，ignition temperature of NTO was found to be higher than that of PETN，RDX，and HMX，whereas it is almost equal to that of TNT，and slightly lower than that of TATB. From this Fig. 2，it can be also deduced that NTO has a lower detonation velocity with respect to that

Table 2 Some physicochemical properties of NTO

NTO	$C_2H_2N_4O_3$	reference
name	3-Nitro-1，2，4-triazole-5-one，5-Nitro-1，2，4-triazole-3-one，5-oxy-3-nitro-1，2，4-triazole（ONTA），nitrotriazolone	[5,17]
CAS No.	932-64-9	−
structural formula		[69]
molecular mass/g·mol⁻¹	130	[21]
density/g·cm⁻³	1.93，1.911，2.06	[27,70−71]
solubility	-soluble in：water，acetone，acetonitrile，dioxin，NMP，DMF，trifluoroacetic acid and DMSO. -limilted solubility in：toluene，chloroform，diethyl ether，ethyl acetate. -insoluble in：dichloromethane.	[19,21]
decomposition temperature/℃	271−273	[72−73]
heat of formation/kJ·mol⁻¹	−101.1	[71]
oxygen balance	−24.6	[73−74]
acidity	a dibasic acid：pK_1=3.76，pK_2=11.25	[71,75]
^{1}H NMR	13.5（H—N adjacent NO_2）and 12.8（DMSO-d_6）	
^{13}C NMR	154.4（C＝O）and 148.0（C—NO_2）（DMSO-d_6）	[20-21]
^{14}N NMR	−34.5.5（H—N），−112.9（N—H），−205.4，−207.4，−243.9	
IR spectrum/cm⁻¹	3212（NH），1714（C＝O），and 1547（NO_2）	
Near IR spectrum/cm⁻¹	6250 and 4550	[19]
Raman IR spectrum/cm⁻¹	1361 and 1329	

of RDX，PETN and HMX，and higher than TATB. On the other hand，it was recently reported that the incorporation of NTO with nitramine filler in plastic bonded explosives increased the resistance against mechanical stimuli or allowed production of the extremely insensitive detonating substances[76].

This powerful compound which does not fall in the traditional classes such as nitrates，nitramines
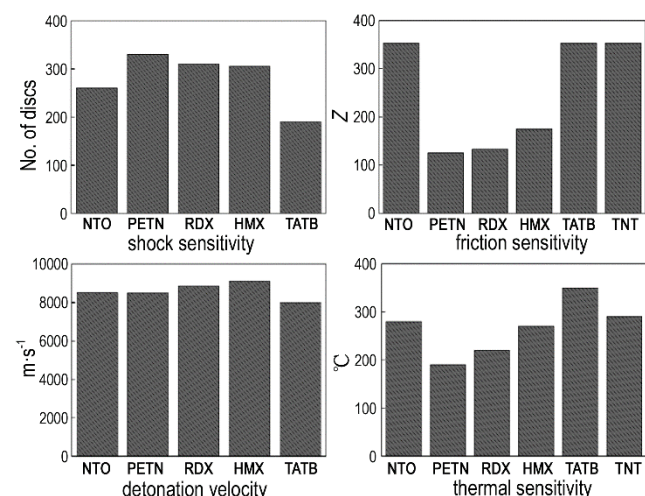
Fig.2 A performance comparison of NTO with those of other high explosives[17,19,21]

andnitrobenzenes，owing to the existence of the >C＝N— chemical group in addition to C—NO_2 linkage. Itexhibits good thermal stability，low-sensitivity to radiation damage，accidental and sympathetic initiation[69,77−78]. The acidic character of NTO and the presence of two reactive（N—H）protons in its molecule allowed the preparation of numerous salts of metals as well as aromatic and aliphatic amines，which can be tailored for a wide range of applications[69,79].In addition，NTO is nitrogen rich and contains other functional groups suitable for interactions such as hydrogen bonding. The derived salts have a number of advantages over nonionic molecules，since these salts display higher density and lower vapor pressure than their respective atomically nonionic analogues[71].

However，NTO presented some drawbacks such as the high solubility in water，the acid reaction by hydrolysis and the large critical diameter needed for the continuation of the detonation[80].The former issue can lead to the increase of NTO amount in industrial wastewater produced during

the manufacturing and processing of its formulations. Recent reports on the toxicity of aqueous NTO on *Ceriodaphniadubia*，northern leopard, frog and rat，cite toxic effect when the concentration reaches and exceeds the range of 1 kg/1000 L[81-82]. For this purpose，a huge amount of work have been doneworldwide in order to find efficient procedures to remove such a harmful explosive from solutions and reduce the risk of environmental contamination[35,67,83].

3.2 Morphology of NTO

Morphologies，sizes（distribution），defects，etc. are the structures above the crystal packing and not intrinsic. They are governed by preparation methods instead of emergent molecular packing in crystal. It is widely accepted that structure，size and morphology have great influence on properties of different materials. The particle size significantly affects various features of particulate materials and offers appropriate indication for quality control and performance. Coarse spherical particles can flow easily and generate high bulk density. Fine particles with suitable morphology，however，are often necessitated to enhance the ballistic parameters and increase the energy output owing to the high surface area[13]. In addition，some authors reported that flow properties such as wettability，packability，and compatibility can be increased to a great extent once spherical particles are used[84]. Consequently，such physical characteristics play vital role in achieving insensitivity，solid loading and mix fluidity in processing and high performance of EMs. One approach to decrease the sensitivity towards mechanical stimuli concerns the alteration of particle size and morphology to cubic or spherical desired morphology，which can be reached by appropriate crystallization method along with suitable operational conditions[48,85-86].

The conventional process of NTO preparation from semicarbazide-hydrochloride in two steps gives rise to rod-like morphologythat is non-spherical in nature，which readily agglomerates and eventually becomes sensitive to unexpected shock. Large-scale production of NTO involves crystallization from water，and this yields irregular rods and jagged crystals. This undesired irregular morphology leads to high viscosity，poor processability and consequently reduces solid loading. This may create issues with explosive formulations，where adverse morphology and size generate handlings difficulties and formulation may be highly viscous and not easy to pour. Thus，water can only be utilized to purify the products and not for obtaining good morphology. For that purpose，several authors have tested various procedures to produce a desired NTO morphology （Table 3）.

Collignon，as one of the pioneers in the crystallization of crude NTO，studied a way for obtaining spheroidal NTO after its crystallization from aliphat-

Table 3 Someprocedures to produce different morphologies of NTO

method	influencing factors	key points	morphology	co-solvent	comment	Ref.
cooling recrystallization	concentration，volume ration，agitator configuration，speed	cooling rate	spherical	water/1-methyl2-pyrolidone	bulk density：0.65-1.15 g·mL^{-1} size：10-200 μm	[48,87-88]
water/oil micro-emulsion	temperature，ratio solvent/antisolvent	surfactant	spherical	n-alkanol	size：10-30 nm	[89]
freeze drying into liquid	concentration，temperature	nozzle diameter and freeze temperature	grids	polyoxyethylenealkylphenol ether	particle size：70-90 nm	[90]
rapid expansion of supercritical solution	concentration extraction temperature and pressure，nozzle size，flow rate	selection of proper solvent	needle-like	–	particle size：540 nm	[91]

ic alcohols containing 1 to 4 carbon atoms or their admixture with water[92]. The solution was heated from 40 ℃ to a boiling temperature of alcohol followed by a fast cooling（6−20 ℃·min⁻¹）under stirring. Spheroidal particles of NTO were recovered at 5−10 ℃. Similar author used a method of crystallization from water with the addition of a surfactant（perfluorinated salts of aliphatic compounds）and methylcellulose in order to form spheroidal NTO[40].

Some authors reported that crash precipitation from DMSO could provide more suitable crystal morphologies. Dissolution of NTO in DMSO and subsequent injection through an opening smaller than 0.7 mm into dichloromethane gives rise to NTO as finely divided particles with surface area of the order of 5.7 m²·cm⁻³[19].

Kim produced spherical NTO by cooling crystallization using co-solvent N-methyl-2-pyrrolidone（NMP）and water[87]. They found that the cooling rate of 10 ℃·min⁻¹ gave better results. It was reported that the mass ratio of NTO/NMP affected the morphology of NTO. Porous particles with cracks and fissures were generated when the ratio is over 0.6. From the different tested mixtures, the combination water/NP=1.0, NTO/NMP=0.39 provided the most advantageous morphology. Furthermore, it was established that the water quantity in the mixture with NMP affected the diameter and the morphology of the recrystallized NTO[93]. The size of particles had an average diameter of 50−220 μm, which depended proportionally on the content of water in the mixture.

Similar approach based on water/NMP mixture was used by Vijayalakshmi[48]. They focused on the synthesis of spherical NTO by rapid cooling crystallization and optimized the crystallization process to achieve fine and spherical particles. They mentioned that higher agitation speed and cooling rate lead to the relatively fine particles. They revealed also that spherical NTO possessed about 40% reduction in viscosity with respect to the conventional jagged and rod type ones. These authors also tried to recrystallize NTO from other solvents, such as aliphatic al-

cohols and their admixtures with water. It was pointed out that none of these latter solvents appeared to adequately obtain better morphology. The crystallized NTO granules, in this case, were partly rounded.

Recently, the Trzcinski group prepared spherical particles of NTO with diameters ranging from 50 μm to 500 μm using a water/NMP mixture（H₂O/NMP=60/40 V/V, cooling rate 1 K·min⁻¹）[88]. The obtained NTO was tested in the formulations containing DNAN（2，4-dinitroanisole）or TNT with RDX. More recently, the similar research group have investigated the effect of addition of different surfactants to the mixture water/NMP [14]. The authors demonstrated that the system NTO/H₂O/NMP/Polyvinyl-alcohol（9−10 / 80 / 20 / 0.008−0.1）at 5−15 ℃ provided desirable morphology of NTO. The obtained product had a high bulk density and presented good resistance to mechanical stimuli, such as friction（353 N）and impact（minimum sensitivity equal to 13 J）.

Similar to themorphology, the particle size of EMs also owns a vital role to achieve good performance in energetic material formulation, since it affects packing density, porosity, cohesion, flowability, and interaction with fluids/binders. Nanosizing of EMs leads to a large available surface area and consequently better heat transmission. There are other advantages of using nanoenergetic materials（NEM）such as improving insensitivity, decreasing thermal decomposition temperature and nano-melting point effect. These NEM may exhibit somewhat faster reaction compared to conventional micron sized ones.

Yang[90] produced nano-NTO by employing spray freezing in liquid method from 90% pure NTO. The obtained nano particles showed an averagesize of 70−90 nm with elongated morphology. These authors compared the thermal decomposition as well as the impact sensitivity of both nano-NTO and micro-NTO. They concluded that the decomposition of nano-NTO occurred at a lower temperature and it is less sensitive to impact stimuli with respect to micro-NTO.

Wang et al. utilized a reverse microemulsion of solvent evaporation technique to produce nanoscale NTO[89]. An *n*-alkanolwas employed as a co-surfactant. The mass ratio between surfactant and co-surfactant was 7∶1 and the water content of the solution was 24%. The experiment was performed at 298−303 K under a vacuum between − 0.6 and −0.85 MPa. The particle size 10−30 nm was obtained.

3.3 Crystal Structures of NTO

Two polymorphic modifications are recognizedfor crystalline NTO. Lee and Gilardi reported the detailed methodologies to prepare these forms[94]. The first polymorph，α-from，was produced by slow cooling of a hot solution of NTO in various solvent（such as water）followed by refrigeration. The obtained crystals appeared as long needles，which shatter when cut perpendicular to the crystal axis. This form is considered as the most stable but tends to twinning，and that is the reason why parameters of its crystal structure were obtained quite recently. The α-form belongs to the triclinic space group P_1 and contains eight molecules in acell unit. Experimental analysis for α-NTO（with density of 1.903 g·cm⁻³） was carried out at 223.2 K by X-ray diffraction method. It was found that molecules in the NTO crystals form ribbons，and are connected by a net hydrogen bonds and weak *van der Waals* interactions[95]. The second form，β-polymorph，was prepared by recrystallization from methanol or a mixed ethanol/dichloromethane solvent. It was mentioned that β-NTO remained stable for six month after which it decomposed. The unit cell of β-NTO is monoclinic of the space group $P2_1/c$ with four molecules in the unit cell，where each molecule is linked to other by four hydrogen bonds. At ambient conditions the β-NTO （with density of 1.876 g·cm⁻³） is less dense than α-NTO[96]. The lattice parameters of the two polymorphs are depicted in Table 4[17,95,97].

Bolotina et al. have investigated the effect of temperature from 100 K to 298 K on the crystal structure of the metastable β-NTO using single-crystal X-ray diffraction techniques[96]. They reported that the thermal expansion occurred in a plane，which is

almost perpendicular to the planes of all NTO molecules. The crystal lattice indicated anharmonicity of the atomic thermal motion. The similar research group reported the crystal structure of α-NTO at 298 K[28]. They exhibited that α-form crystalized as a four component triclinic twin with four crystallographic independent molecules in the symmetric unit. Hydrogen bonding created two independent ribbons in the crystal structure.

Table 4   The crystal lattice parameters of α- and β- polymorphs of NTO

crystal polymorph	α-NTO	β-NTO
crystal system	triclinic， 8 molecules/cell	monoclinic， 4 molecules/cell
space group	$P1$	$P2_1/c$
a/Å	5.12	9.310
b/Å	10.30	5.450
c/Å	17.90	9.030
α/(°)	106.7	90.00
β/(°)	97.70	101.46
γ/(°)	90.20	90.00
density /g·cm⁻³	1.903	1.876

Recently，Rykounov has studied the effect of finite pressures on the structural and thermodynamic properties of the two polymorphic forms using the *ab initio* approach[95]. No significant structure was found under pressure of 50 GPa for α-NTO，whereas β-NTO showed a structural change even at 17.5 GPa. In the work of Wu et al.，the structural properties of β-NTO have been investigated under hydrostatic pressure of 0−160 GPa[98]. The *b* and *c* parameters are sensitive to *van der Waals* interactions. The structure was the stiffest in *a* direction in the whole pressure range. It was revealed that NTO decomposesat 150 GPa by breaking of N—O bond in nitro group，and polymerized by forming a new N—H covalent bond between one nitrogen atom in the ring and one hydrogen atom connected to the ring in another molecule.

4 NTO-based Co-crystals

A relatively new concept that is receiving sub-

stantial interest to tailor the physicochemical properties of EMs is *co-crystallization*[99]. Although nowadays established within the pharmaceutical field, as a means for enhancing the solubility, bioavailability, physicochemical and stability properties of active pharmaceutical components without modifications in their chemical structure[100−101], co-crystallization is now at an early-phase of development within the field of EMs, but it is starting to demonstrate consequent promise. The latter strategy can improve the comprehensive properties without sacrificing the energy output. More and more energetic co-crystals （ECC） are being produced, opening a road to new high EMs with required features[99,102−104]. ECC are crystals encompassing two or more neutral molecular compounds in which at least one is energetic in a certain ratio through non-bonded interactions. The intermolecular interactions and hydrogen bonds formed between the components of co-crystals help to achieve prominent features than their respective constituents. Recent research activities on synthesis of new EMs by combining a sensitive and a less sensitive material to obtain better packing density, desired morphology, higher performance and increased safety through the process of co-crystallization are reported[105]. To date, several ECC have been synthesized experimentally and calculated theoretically. For instance, 17 co-crystals of TNT with various aromatic or heterocyclic co-formers have been prepared by Landenberger and Matzger and demonstrated an alteration of key characteristics such as melting point, decomposition temperatures, and density[106]. Similar authors produced various HMX co-crystals and revealed a tremendous decrease in sensitivity compared to pure HMX[107]. Other co-crystals have been achieved such as those of benzotrifuroxan （BTF） [108−109]，2，4，6，8，10，12-hexa-nitrohexaazaisowurtzitane （CL-20） [110−112]，ethylenedinitramine[113−114], diacetonediperoxide[115−116]，azole derivatives[117−118]，among others.

Azole-based EMsare of potential interest for co-crystallization investigations as they exhibit relatively good hydrogen bond donor or acceptor mole-

cules. NTO is an example of such azole derivatives.

Lin et al. explored NTO as co-crystal former to co-crystallize with HMX[15]. They calculated the bonding energies, thermodynamic properties, detonation properties, and thermal stability using density functional theory methods. Furthermore, they studied the crystal structure of HMX/NTO co-crystal using Monte Carlo simulation and first principles methods. The authors demonstrated that the intermolecular interactions were governed by CH···O and NH···O interactions, as well as O···O and N···O weak interactions. The co-crystal formation was exothermic with low entropy. The change of Gibbs-free energy was negative at 300 K, showing that lower temperature allows the formation of HMX / NTO co-crystals. It was also exhibited that the detonation velocity of the co-crystal was lower than that of HMX, and its thermal stability meets the requirement of high energy density materials. Recently, Song et al. employed a molecular dynamics method to investigate the bonding energies associated with the co-crystallization of NTO with either α- and β-HMX[119]. They exhibited that HMX/NTO with low molecular rations （2∶1，1∶1，1∶2，1∶3），are the most stable. The binding energies of such co-crystal arelarger than those of HMX/TATB and HMX/FOX-7 co-crystals. It was shown that C＝O···H—C hydrogen-bonding interactions were the main driving force for co-crystallization. In addition, the β-form was preferred when molecules in NTO super-cellswere substituted with HMX, as in α-form. The authors revealed that the increase of HMX proportion would increase the denotation velocity and pressure to the detriment of the sensitivity. In another work, Li et al. prepared a co-crystal of HMX/NTO in a molar ratio of 1∶1 by solvent/antisolvent method[120]. It was shown, as mentioned in Table 5, that the morphology of the co-crystal is different from its respective co-formers. The produced co-crystals possessed low sensitivity to impact and friction compared to HMX.

Recently，Wu et al. reported the co-crystallization of NTO with a nitrogen-rich compound 5，6，7，8-tetrahydrotetrazolo ［1，5-*b*］［1，2，4]-triazine

（TZTN）[121]. This latter was chosen as it is a weak base and it could potentially the acidity of NTO. Strong intermolecular NH⋯N and NH⋯O hydrogen-bonding interactions are the primary driving force in the preparation of the energetic-energetic NTO/TZTN co-crystal. As mentioned in Table 5, the co-crystal melts at 156.6 ℃ and increases comparing with TZTN，what is attributed to the hydrogen bonding in the structure. Its exothermic peak shifts to lower temperature with two continuous sharp exothermic process at 177.5 ℃ and 197.9 ℃，respectively，what indicates some changes in the crystal phase. The detonation velocity and detonation pressure of NTO/TZTN co-crystal are 7458 km·s⁻¹ and 23.5 GPa，respectively，a little lower than those of NTO. The co-crystal presents a crystallographic density of 1.665 g·cm⁻³，which is higher than TZTN，

but lower than that of NTO. In another research work, Zhao and Yang[16] have used thedensity functional theory（DFT）to study the effect of hydrostatic pressureof 0−80 GPa on the geometrical and electronic structures of the energetic NTO/TZTN co-crystal. It has been revealed that the increasing of pressure contributed to the increase of interaction force gradually. The stability of such co-crystal has been improved by the formation of five and eight membered rings during external compression. At 4 GPa，the transformation from H-bond $O(1)\cdots H(3)$ to covalent bond contributed to the formation of the eight membered ring. In addition，a new covalent bond is generated between $N(2)$ and $H(4)$ atoms. After 8 GPa，the covalent bond between $O(1)$ and $H(3)$ atoms，$N(4)$ and $H(2)$ atoms intensified the thermal stability of the co-crystal system significantly.

Table 5   Properties of NTO，TZTN and their co-crystal

sample	NTO	TZTN	HMX	NTO/TZTN	NTO/HMX
density /g·cm⁻³	1.93	1.577	−	1.665	1.92
heat of formation /kJ·mol⁻¹	−6.3	499.2	−	481.4	−
detonation velocity /m·s⁻¹	8446	7272	9100	7458	8730
detonation pressure /GPa	33	21.6	37.76	23.5	35.14
exothermic pick/℃	279	197.1	281	177.5，197.9	282.5

In addition to the current method widely employed for the formation of co-crystals such as solution co-crystallization，mechanochemical methods and ultrasounds，a relatively new method, which is the resonant acoustic mixing，has been recently utilized[122]. This latter is revealed to be safe，simple，scalable and is supported by a commercial platform of RAM mixers available through the Resodyn Corporation. This approach was efficiently applied to prepare NTO/4,4-biperidine（BP）co-crystal，where a drop of water is required otherwise a salt is formed[123].

Spontaneous crystallization from solution at room temperature was reported by Lloyd，whichproducesa co-crystal of NTO/BP in 1∶1 molar ratios[124]. It was exhibited that the crystal structure density and detonation velocity of the co-crystal are lower than those of NTO. The co-crystal displayed a sharp exo-

thermic peak at 217 ℃. A sharp endothermic peak was also observed，whichis attributed to the melting of the decomposition products.

In the paper of Hang，a novel energetic co-crystal consisted of CL-20/NTO with different molar ratios was established through substitution method[97]. The geometric structures and the properties were optimized based on the molecular dynamics method. The authors revealed that the co-crystal formed with the molar ratio in 2∶1，1∶1 or 1∶2 showedhigher stability，lower mechanical sensitivity and better safety in comparison to CL-20. The detonation properties and performances of the co-crystals are declined，but they still displayed excellent energy density.

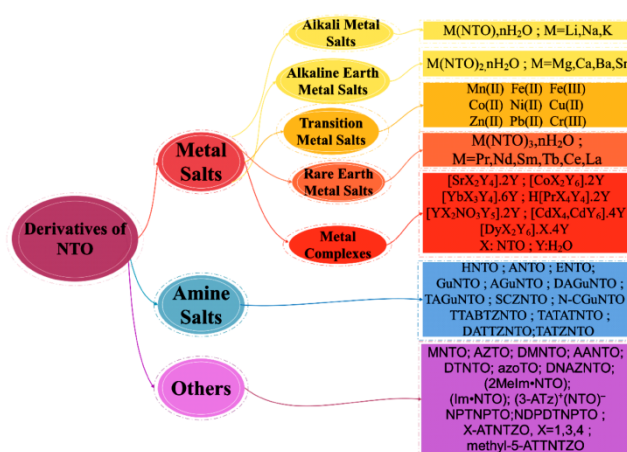# 5 NTO Derivatives

The acidic nature of NTO allows the formation

of a large number of salts with metals, aliphatic and aromatics amines（Fig. 3）[69]. The preparation of NTO salts involves simple acid-base reaction. There are many reports in the literature about the ionization of NTO. The two hydrogen sites in NTO molecule at positions N（2）and N（4）（Table 2）can be ionized to form different derivatives of NTO by changing the nature of the solution. It has been shown that the hydrogen at position 2 is more acidic than that at position 4[19,72].

Several works have been performed until now, where a huge number of NTO derivatives have been reported[17,71-73,79,125-126]. The pioneering works on NTO derivatives have been carried out by Chipen et al. and then completed by a research group from US department of the army and the US department of energy[29]. Commonly, the preparation of amine salts of NTO was achieved by mixing the hot aqueous solution of NTO with a solution of corresponding base. Lee et al. have synthetized seven amino salts of NTO hydrazine(HNTO), ammonia(ANTO), ethylenediamine（ENTO）, guanidine（GuNTO）, aminoguanidine(AGuNTO),diaminoguanidine（DAGuNTO）, triaminoguanidine(TAGuNTO)[70,127]. Furthermore, it has been demonstrated that ANTO and ENTO appeared as potential candidates to be used as explosives[128].

Recently, Singh has deeply reviewed the preparation, characterization, thermolysis and application of more than 50 NTO salts[19]. Various salts are considered insensitive and highly energetic in nature, in addition to other prominent features and potential applications. Salts with high-nitrogen cations such as hydrazine andtriaminoguanidine, are suggested as constituents of gun-propellants[127]. Salts with metals have been assessed as ballistic modifiers and catalysts for solid rocket propellants[129-130].

Other interesting amino-based salts of NTO, that have also been well characterized, are dimethylamine（DMNTO）, 3,3-dinitroazetidine（DNAZNTO）, and 2-azidoethylamine（AANTO）[125-126,131-132]. Another derivative of NTO has been obtained by nitration using fuming nitric acid and acetic anhy-

dride, which is the 2,4-dihydro-2,4,5-trinitro-3H-1,2,4-triazol-3-one（DTNTO）. In this case, the NH group of NTO is substituted by NO_2. It has been found that this new derivative is more sensitive than NTO, but has positive oxygen balance which is an attractive feature from the point of view of its application as an eco-friendly oxidizer in propellant formulations[133].

Fig. 3 A compilation of NTO derivatives reported in literature. SCZNTO：semicarbazidiumNTO；N-CGuNTO：N-carbamoylguanidiumNTO；TTABTZNTO：4,40,5,50-tetraamino-3,30-bi-1,2,4-triazoliumNTO；TATATNTO：3,6,7-triamino-7H-[1,2,4]triazolo[5,1-c][1,2,4]-triazol-2-iumNTO；DATTZNTO：1,5-diamino-1,2,4-tetrazoliumNTO；TATZNTO：3,4,5-triamino-1,2,4-triazoliumNTO；X-ATNTZO：X- Amino- 1,2,4-triazolium-3-Nitro-1,2,4-triazolate-5-one；Methyl -5-ATTNTZO：Methyl -5- Amino- 1,2,4-tetrazolium-3-Nitro-1,2,4-triazolate-5-one；NPTNPTO：5-nitro-2-picryl（2,4,6-trinitrophenyl）-2,4-dihydro-3H-1,2,4-triazol-3-one；NDPDTNPTO：5-nitro-2,4-dipicryl（di-2,4,6-trinitrophenyl）-2,4-dihydro-3H-1,2,4-triazol-3-one[69]

During the past few years, new NTO salts have been investigated as well（Fig.3）. Energetic salts containing either energetic substituted triazolium or tetrazolium cations and 3-nitro-1,2,4-triazolate-5-one anions have been synthesized and characterized by Shreeve's group[71]. 3-Amino-1,2,4-triazolium 3-nitro-1,2,4-triazolate-5-one, 1-amino-1,2,4-triazolium 3-nitro-1,2,4-triazolate-5-one, 4-amino-1,2,4-triazolium 3-nitro-1,2,4-triazolate-5-one, methyl-5-amino-tetrazolium, and 3-Nitro-1,2,4-triazolate-5-one are formed by using NTO as substrate. These energetic salts exhibited good properties in-

cluding relatively high densities，high positive heat of formation and moderate detonation properties，because both cation and anion have the highest nitrogen content which in turn enhanced the density and the detonation characteristics.

The melamine 3-nitro-1，2，4-triazol-5-one salt (MNTO) was synthesized and characterized by Najafi et al.[134]. It has been found that it possesses a critical temperature of thermal explosion higher than that of NTO. In 2011，they further performed a study on thermal behavior of MNTO. It reveals that MNTO could be used invarious applications which requires high insensitivity，thermal stability，and nitrogen content[135].

Wallace et al. have reported the synthesis of new azo and azoxy compounds *via* electrochemical reduction of nitrotriazoles in aqueous media using nitrotriazolone (NTO) and nitrotriazole (NTr) as representative substrates. Reduction of NTO produces mainly solid azoxytriazolone (AZTO)，with azotriazolone (azoTO) and aminotriazolone (ATO) as minor products[136]. These compounds，which exhibited greater thermal stability than NTO，have been shown to be of interest as new green high-nitrogen compounds for use as insensitive high explosives[137]. Before that，Cronin et al. had reported on the formation of AZTO by electrochemical reduction of nitrotriazolone (NTO) in acidic aqueous solution[138].

In another work，Ren et al. have synthesized an ionic compound (3-ATz)⁺ (NTO)⁻ by the reaction of 3-amino-1，2，4-triazole (3-ATz) with NTO in ethanol[125]. The obtained product has a good oxygen-balance，a higher chemical stability and consistency to be employed in propellant and explosive formulations.

Monopicryl and dipicryl derivatives of NTO (5-nitro-2-picryl (2，4，6-trinitrophenyl)-2，4-dihydro-3H-1，2，4-triazol-3-one and 5-nitro-2，4-dipicryl (di-2，4，6-trinitrophenyl)-2，4-dihydro-3H-1，2，4-triazol-3-one) have been synthesized by the treatment of NTO with picryl fluoride in 1-methyl-2-pyrrolidinone (NMP)at room temperature[139]. In ref.[140]，authors have investigated the theoretical investigation

of two classes of NTO-picryl derivatives including 12 constitutional isomers. It has been revealed that all constitutional isomers are endothermic in nature，and have higher detonation performance than NTO.

Because of the lack of detonation data of several amine salts (HNTO，ANTO，GuNTO，AGuNTO，DAGuNTO，TAGuNTO)，Zhang[73] have recently synthesized and characterized these latter in addition to six new salts，which are N-carbamoylguanidinium，semicarbazidium，1，5-diamino-1，2，4-tetrazolium，3，4，5-triamino-1，2，4-triazolium，3，6,7-triamino-7H-[1，2，4]triazolo[5，1-c][1，2，4]-triazol-2-ium，and 4，40，5，50-tetraamino-3，30-bi-1，2，4-triazolium. The reported results showed that all the energetic salts except TAGuNTO exhibited excellent thermal stabilities with decomposition temperatures up to 200 ℃. Moreover，they have established that HNTO had excellent properties such as thedetonation velocity of 9575 m·s⁻¹，which is comparable to that of CL-20，and the friction sensitivity of 360 N with a decomposition temperature of 203 ℃. It is also found compatible with most of potential EMs，what making HNTO a highly promising energetic material for composite explosives and propellants.

More recently，Szala have synthesized two new salts of NTO，which are the 2-methylimidazole (2MeIm·NTO) and Imidazole (Im·NTO) by dissolving NTO in DMSO and heating the solution to 40 ℃ for imidazole and 50 ℃ for 2-methylimidazole[79]. They have reported that both salts are stable up to 200 ℃ and present lower sensitivity for mechanical stimuli than TNT. Detonation velocity and pressure are similar to those of TNT and much lower than that estimated for NTO. Furthermore，2MeIm·NTO has methyl group with three protons which arranges the molecules in crystal better than the parent imidazole. Newly described NTO imidazole salts may have lower acidity than appropriate cocrystals.

6　NTO-based Formulations

Researchers are exploring different approaches to fulfill the increasing requirements of EMs that im-

part high performance, enhanced mechanical prop-erties, prolonged life time, less vulnerability, and negligible environmental effects during manufactur-ing, processing, handling, transport, storage, us-age and disposal[2,8]. Efforts are being made all over the world to develop modern/furistic EMs-based sys-tems meeting the previously mentioned challenges. Safety aspects of high-energy materials are one of the key factors of research activities in this field. Thus, compounds with high energy combined with less sensitivity are sought for. Luckily, the NTO is such a component with performances comparable to that of RDX and insensitivity comparable to that of TATB. Its thermal stability is also high and decom-poses exothermically at around 272 ℃[18]. NTO is currently widely employed in several formulations such as explosive fillings：melt-cast, cast-cured plas-tic bonded explosives（PBX）and pressed PBX, gas generators for automobile inflator air bags systems, etc.[2,18−19,21,76,79,82,110,141]. The salt derivatives of NTO are also found insensitive and are tested for several explosive formulations, ingredient of gun-propel-lants, modifier and catalyst for rocket propellant[19,73,79]. Nevertheless, despite the number of prepara-tion methods and characteristics of several NTO salts existing in the open literature, the reports on the applications of these EMs are either meagerly ac-cessible or hidden in classified reports.

NTO-based explosive formulations have been considered for a variety of applications. Smith and Cliff have reviewed the formulations containing NTO developed by UK, Swiss and Norwegian, Ger-man and Canadian and that performed at SNPE（French）[21,142]. Mukundan et al. have proved that NTO-based presses and cast-cured explosive formu-lations exhibited superior mechanical and thermal properties, and more importantly they are insensi-tive[41]. NTO has been used in PBX based on silicon rubber and it has been revealed that its activation en-ergy and onset temperature are relatively high（267.0 ℃）, which reveals better thermal stability than other PBXs[143]. The Société Nationale des Pou-dresetExplosifs（SNPE）, France, has reported

B-2214 based on an inert binder, HMX and NTO（12% and 72% respectively）for missile warhead. It was demonstrated that this formulation is less sensi-tive and more efficient that Composition B（Hexol 60/40）[2]. Baudin et al. have studied the shock-to-det-onation transition（SDT）and its modeling for cast-cured PBX containing HMX, RDX and NTO and they have compared it to pressed one[144]. They have revealed that a cast-cured PBX is not porous in con-trary to a pressed PBX and the hot-spots are mainly located at the grain-binder interface in case of cast-cured PBX, leading to a different burning behav-ior during shock-to-detonation transition. Moreover, it has been revealed that cast-cured PBX containing HMX, RDX and NTO does not exhibit any desensiti-zation when submitted to double shock waves.

More recently, Zeman's group has reported a new PBX based on cis-1,3,4,6-tetranitrooctahydro-imidazo-[4,5-d]imidazole（BCHMX）and NTO, boned by polydimethylsiloxane binder（44/44/12 mass fraction）. These researchers revealed that this insensitive formulation appeared as a good candi-date for LOVA explosives with high detonation pa-rameters, good thermal stability and better mechani-cal properties[76]. In another work, Tappan et al. have prepared a formulations based on 3,3′Diami-no-4,4′-Azoxyfurazan（DAAF）and NTO to evalu-ate their detonation performance. The obtained prod-uct presented better properties such as a smaller fail-ure diameter, lower shock sensitivity, higher density and detonation pressure[141]. Belaada et al. have pre-pared a melt-cast composition based on NTO and FOX-7[145]. The obtained composition exhibited good rheological features and the casting process may be performed at a temperature range of 85−90 ℃. The sensitivities to impact, shock wave, jet attack and fast heating determined were lower than those of TNT. It is indicated that such composition is promising as a main charge filling destined for insen-sitive munitions.

In the recent years, TNT has been substituted by NTO in IMX-101 formulation, which contained 43.5% 2,4-dinitroanisole（DNAN）, 19.7% NTO,

and 36.8% nitroguanidine, and has been qualified for use by U.S. National Service Authority[146]. Other formulations such as IMX-104（OSX-7，DNAN/NTO/RDX）and PAX48（OSX-8，DNAN/NTO/HMX）have been reported，where NTO was revealed as alternative to replace RDX in large caliber munitions，and considered safer for troops due to their lower likelihood for unintended explosions[67,147].

A number of NTO salts were considered for explosive formulations[19]. Recent studies concluded that some salts are likely to show interesting properties such as decomposition temperature，densities，detonation pressure and detonation velocities [73,79]. Furthermore，in addition to the low environmental impact，they are considered more compatible with most of the commonly employed or potential energetic compounds such as TNT，CL-20，TNAZ，TKX-50，Al，ammonium perchlorate，etc. Therefore，such salts are promising candidates for use in future composite explosives and propellants.

On the other hand，various NTO salts have been tested in propellant compositions as ballistic modifiers. Singh et al. have assessed the effect of NTO as catalysts for HTPB/AP propellants. Very promising results have been achieved[130,148]. Some authors have also demonstrated the potential of NTO to substitute AP（heat of formation of -296.0 kJ·mol^{-1}）in composite solid propellants since NTO presents higher heat of formation（-276.56 J·mol^{-1}）and its combustion is environmentally friendly[19].

However，it is worthy to note that much work is needed to be done on the effects of these salts on the processing parameters，stability and aging，before its real usage. In addition，various theoretical calculations should be experimentally validated to check the effect of such components on the total energy as well as specific impulse. The extension of these investigations to other composite solid propellants，composite modified double base propellants，and explosives may be considered. Furthermore，new formulations based on NTO co-crystals will certainly bring new insight in the field.

7　Conclusions

The currently developed substitutes of the conventional EMs such as NTO need optimization to fully satisfy the requirements of ideal high EMs. Thus，high-performing energetic ingredients with better safety characteristics are a top priority internationally and need further endeavor to reach their aim. In the present report，comparative strategies to produce NTO as well as the methodologies to modify its particles morphology and size have been investigated. It has been found that some recent synthesis methods are efficient and the prepared NTO had better yields than the conventional methods. The use of spherical NTO is vital in realizing high-energy formulations with high physicochemical properties and better performance. The existing literature on newer form of NTO including derivatives and co-crystalshas been collected. Various recent NTO derivatives present tremendous advantages such as high performance，better stability，insensitivity，compatibility and high density，and are sufficiently assessed in different propellant and explosive formulations. Further improvement on the properties of NTO has been reached by the preparation of co-crystals，and such approach provides promising way to tune the NTO physicochemical features and performance.

For the near future，energetic formulations containing NTO，its derivatives or co-crystals are expected to advance the state-of-the-art of EMs field. New NTO derivatives and co-crystals based formulations with improved safety and performance features，compared with the corresponding conventional formulations，are very interesting and may play a prominent role in the future of high EMs，propellants and weaponry.

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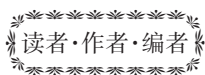
中国兵工学会火工烟火专业委员会第二十届学术年会征文通知

为促进我国火工烟火行业的创新发展，紧跟世界火工烟火前沿技术和新兴技术发展趋势，加强科技人员间的学术交流与信息沟通，提高研究水平，经研究，定于2019年四季度召开中国兵工学会火工烟火专业委员会第二十届学术年会。现将会议征文有关事项通知如下：

一、征文内容

1. 国内外火工品及相关药剂、烟火剂的基础理论和关键技术；2. 国内外火工品、爆破器材、烟火器材的发展动态、现状及趋势；3. 国内外火工品及相关药剂设计的新理论、新方法、新技术；4. 国内外火工品及相关药剂制造的新工艺、新材料、新设备；5. 火工品及相关药剂测试、分析、计量的新理论、新技术及新仪器；6. 火工品安全性、可靠性评估新理论、新方法、新技术；7. 火工烟火行业标准化的研究、标准探讨、经验交流、发展趋势；8. 信息技术在火工品及相关药剂管理、设计、仿真、试验、工艺、评估、数据库建设中的应用；9. 火工品机械化、自动化、智能化先进制造技术；10. 其它具有一定创新价值的技术、产品或具有较大意义的军民融合技术。

二、征文要求

1. 研究成果具有较高的理论水平或应用价值；2. 论文未在国内外正式出版物上发表过，文责自负；3. 提交的论文为非密，须通过所在单位的保密审查；4. 论文格式按照科技论文标准规范，要求用 Word 2007 以上版本软件排版；5. 论文格式及排序：题目，作者名，单位名，所在地，邮编，中文摘要，中文关键词，正文，参考文献，作者简介。

三、征文时间

征文截至时间为2019年6月20日。优秀论文将推荐到《火工品》期刊发表。

学术年会召开的具体时间和地点另行通知。

四、联系方式

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<div align="right">中国兵工学会火工烟火专业委员会
2019年3月18日</div>