



## **A Study of the Detonation Properties, Propellant Impulses, Impact Sensitivities and Synthesis of Nitrated ANTA and NTO Derivatives**

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**Abstract:** Nitrated derivatives of 5-amino-3-nitro-1,2,4-triazole (ANTA) and 3-nitro-1,2,4-triazol-5-one (NTO) were theoretically characterized with respect to their performance as high explosives and rocket propellants. The detonation velocity and the detonation pressure of the derivatives, calculated with EXPLO5 software, were at the same level or slightly above the performance of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX). The results showed that compositions of 1,3,4-trinitro-1,2,4-triazol-5-one and glycidyl azide polymer (GAP) could give specific impulses just above 2600 m/s in rocket propellants. The sensitivities of the derivatives were evaluated using their heats of detonation, CHNO-ratios, free space in the crystal lattice and N–NO<sub>2</sub> bond dissociation energy. The stability and sensitivity of several of the derivatives could be poor due to the low N–NO<sub>2</sub> bond dissociation energies. The N–NO<sub>2</sub> bond dissociation energies in the derivatives were calculated to be between 41 and 296 kJ/mol when the M06-2X/6-311+G(2d,p) functional was used. Synthetic routes for the most stable derivatives were proposed. In addition, preliminary studies of the chloride-assisted nitrolysis of NTO were performed. The infrared spectrum of the NTO derivative indicated that N–NO<sub>2</sub> bonds were formed.

**Keywords:** detonation properties, propellant impulses, DFT, NTO, ANTA

## 1 Introduction

In solid rocket propellants where high-performance is required, ammonium perchlorate (AP) is commonly used as the oxidizer. The disadvantage of this type of propellant is that it generates thick smoke containing hydrochloric acid during combustion. In addition, AP propellants are relatively sensitive to impact and friction [1]. Propellants based on nitramines such as RDX are characterized as minimum-smoke propellants, but their performances are inferior to AP propellants. NTO (3-nitro-1,2,4-triazol-5-one) and ANTA (5-amino-3-nitro-1,2,4-triazole) are two nitrogen heterocyclic energetic compounds with low sensitivity. Both of them have high density, and their detonation pressure and velocity are comparable to RDX. Therefore, NTO is used in low sensitivity explosive compositions [2], but due to the negative oxygen balance and enthalpy of formation of ANTA and NTO, these compounds release a significantly smaller amount of heat than RDX in a detonation. The negative oxygen balance also implies that neither ANTA nor NTO is suitable as the main oxidizer in minimum-smoke rocket propellants since the impulse will be too low for application in tactile missiles.

Zbarsky and Yudin studied the nitration of 1,2,4-triazol-5-one under various conditions and found that highly sensitive products could be formed if a nitro group was substituted onto a nitrogen atom in the 1,2,4-triazole heterocycle [3]. Jadhav *et al.* nitrated NTO to 1,3,4-trinitro-1,2,4-triazol-5-one. This compound has an oxygen balance of +21%, and a relatively low impact sensitivity (24 J) compared to RDX (7.5 J) [4]. Dipold *et al.* nitrated ANTA to 5-nitramino-3-nitro-1,2,4-triazole which was found to be more impact and friction sensitive than RDX [5]. There have been several theoretical characterization studies of 1,2,4-triazole derivatives [6-9]. Turker and Atalar investigated 1,2,4-triazol-5-one where a nitro group was substituted at a carbon or nitrogen atom in the heterocycle [10]. They found that there were significant differences in bond dissociation energy depending on the position of the nitro group. Ravi *et al.* calculated the explosive performance, Mulliken charges and band gaps of 70 NTO derivatives substituted with CH<sub>3</sub>, NH<sub>2</sub>, NO and NO<sub>2</sub> groups [11].

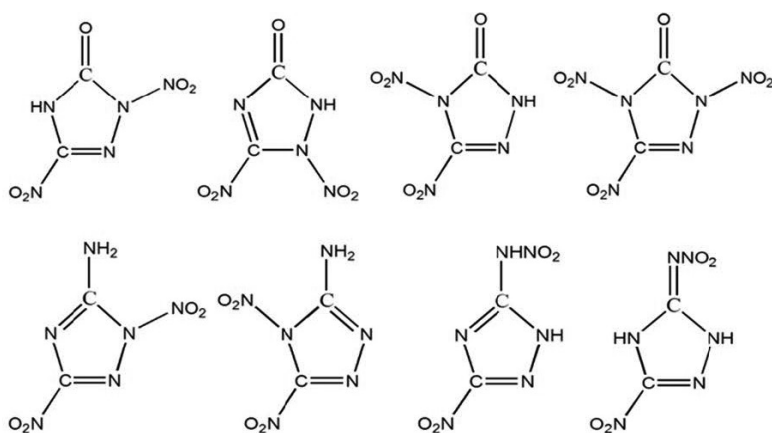
In order to determine the explosive and rocket propellant performance of an energetic material, knowledge of the enthalpy of formation of the compound in the solid phase and the density is essential. These two parameters can be calculated by quantum chemical methods [12-15]. Furthermore, a number of additional parameters such as bond dissociation energies, Mulliken charges and electrostatic potentials, that can provide an indication of the impact sensitivity, can also be computed [16-20]. However, so far no general theory has been

established enabling the impact sensitivity to be accurately calculated for a wide range of energetic molecules [21-23].

One way to improve the performance of ANTA and NTO is to nitrate them further in order to increase the oxygen balance and the enthalpy of formation. Therefore, the objective of this study was to theoretically characterize various nitrated derivatives of NTO and ANTA with respect to performance as high explosives and as rocket propellants. The correlation between impact sensitivity and heat of detonation, free space per molecule in the crystal lattice, bond dissociation energies and CHNO-ratios of these derivatives are discussed. The N-NO<sub>2</sub> and C-NO<sub>2</sub> bond dissociation energies were computed by using the DFT functionals B3LYP and M06-2X, and the complete basis set method CBS-4M. An alternative synthetic route for NTO derivatives was studied.

## 2 Theory and Methods

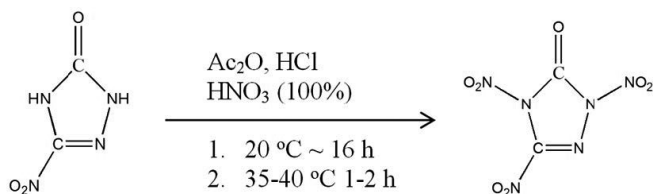
ANTA, NTO, RDX, 1,3,5,7-tetranitroperhydro-1,3,5,7-tetrazocine (HMX) and 2,4,6-trinitrotoluene (TNT) were used as reference compounds in terms of detonation and propellant performance, and sensitivity. The molecular structures of the nitrated NTO and ANTA derivatives are shown in Figure 1.



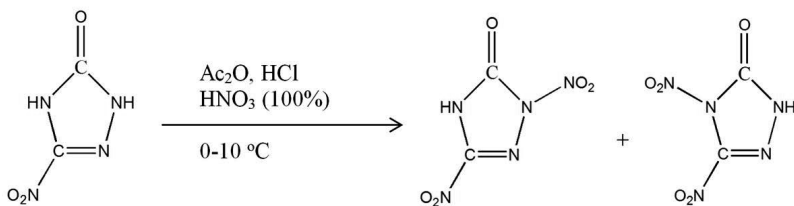
**Figure 1.** Molecular structures (upper line from left to right) of 1,3-dinitro-1,2,4-triazol-5-one, 2,3-dinitro-1,2,4-triazol-5-one, 3,4-dinitro-1,2,4-triazol-5-one, 1,3,4-trinitro-1,2,4-triazol-5-one, (bottom line from left to right) 5-amino-1,3-dinitro-1,2,4-triazole, 5-amino-3,4-dinitro-1,2,4-triazole, 5-nitramino-3-nitro-1,2,4-triazole and 5-nitrimino-3-nitro-1,2,4-triazole.

## 2.1 Synthetic routes

Jadhav *et al.* synthesized 1,3,4-trinitro-1,2,4-triazol-5-one by dissolving NTO in a mixture of hydrochloric acid (HCl), acetic anhydride (Ac<sub>2</sub>O) and fuming nitric acid (HNO<sub>3</sub>) (Scheme 1). The mixture was stirred overnight at room temperature and then heated (35-40 °C) for 1-2 hours, poured over crushed ice and filtered off [4]. Pagoria and co-workers synthesized dinitrourea energetic materials by nitrating hydrochloric acid salts of urea compounds [24], whereas Cliff *et al.* reported the use of zinc chloride and ammonium chloride in the nitration step in the synthesis of nitramines [25]. In these nitrating reactions, the chloride is oxidized by nitric acid to an electropositive chlorine cation and the secondary amine is converted into a chloramine. The nitramine is then formed by an electrophilic attack of the nitronium ion on the nitrogen atom in the chloramine [26]. In our work, we investigated if zinc chloride, ammonium chloride or sodium chloride might be used as a chloride source instead of hydrochloric acid in the nitrolysis of NTO.



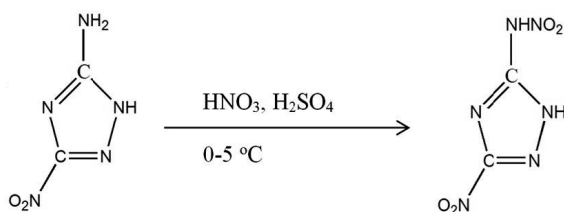
**Scheme 1.** Synthetic route for 1,3,4-trinitro-1,2,4-triazol-5-one [4].



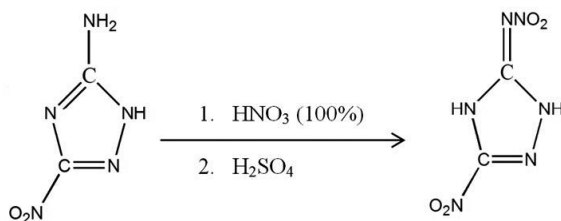
**Scheme 2.** Proposed synthetic route for 1,3-dinitro-1,2,4-triazol-5-one and 3,4-dinitro-1,2,4-triazol-5-one.

Based on the synthetic routes to other nitrourea molecules, mono-substituted NTO derivatives may be obtained if the reaction temperature is kept between 0 °C and 10 °C (Scheme 2) [24]. 5-Nitramino-3-nitro-1,2,4-triazole was synthesized by Dippold *et al.* according to the synthetic route shown in Scheme 3 [5]. Klapötke and co-workers synthesized 5-aminotetrazole nitrate from 5-aminotetrazole and nitric acid [27]. By mixing the product with concentrated

sulphuric acid they obtained 5-nitriminotetrazole. A similar strategy might work for the synthesis of 5-nitrimino-3-nitro-1,2,4-triazole (Scheme 4). When NTO is dissolved in concentrated nitric acid reactive by-products are formed [3, 28]. If ANTA is mixed with concentrated nitric acid similar reactions might occur and the proposed route for 5-nitrimino-3-nitro-1,2,4-triazole (Scheme 4) would need to be modified. Thus, Scheme 3 may be the first step in a synthesis towards 5-nitrimino-3-nitro-1,2,4-triazole. A chloride-assisted nitrolysis could also be an alternative.



**Scheme 3.** Synthetic route for 5-nitramino-3-nitro-1,2,4-triazole [5].



**Scheme 4.** Proposed synthetic route for 5-nitrimino-3-nitro-1,2,4-triazole.

## 2.2 Enthalpy of formation of the solid

According to Hess' law it can be stated that:

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{sub} \quad (1)$$

where  $\Delta H_f(s)$  is the enthalpy of formation of the solid,  $\Delta H_f(g)$  is the enthalpy of formation of the gas, and  $\Delta H_{sub}$  is the sublimation enthalpy. The enthalpy of formation of the gas is calculated by applying the method of atomization energy, to read:

$$\Delta H_f(g) = H_{molecule}^0 - \sum H_{atoms}^0 + \sum H_{f,atoms}^0 \quad (2)$$

where the term  $\sum H_{f,atoms}^0$  is added since  $\Delta H_f(g)$  in its most stable state is given

by definition relative to the elements [13, 29, 30].  $H^0_{molecule}$  and  $H^0_{atoms}$  at 298 K are calculated by using the complete basis set method CBS-4M. This method is a re-parameterization of the original CBS-4 and contains additional empirical correction terms.  $\sum H^0_{f,atoms}$  is taken from NIST [31]. An empirical model based on the electrostatic potential (ESP) was used to predict the heat of sublimation of the energetic compounds [12, 32]. It has been proposed that non-covalent intermolecular interactions may be related to the electrostatic potential, which is defined as:

$$U(\vec{r}) = \sum_{i=1}^N \frac{Z_i}{\|\vec{R}_i - \vec{r}\|} - \int \frac{n(\vec{r}')}{\|\vec{r}' - \vec{r}\|} d\vec{r}' \quad (3)$$

where  $Z_i$  is the charge on nucleus  $i$ ,  $\vec{R}_i$  is the position of the nucleus  $i$  and  $n(\vec{r})$  is the electron density of the molecule [33, 34]. Politzer applied a balance parameter,  $v$ , which describes the degree of positive and negative balance of the ESP on the isosurface having an electron density of 0.001 electrons/Bohr<sup>3</sup>:

$$v = \frac{\sigma_+^2 \sigma_-^2}{(\sigma_+^2 + \sigma_-^2)^2} \quad (4)$$

where  $\sigma_+^2$  and  $\sigma_-^2$  are defined as the variances of the positive and negative potentials on the molecule isosurface with an electron density of 0.001 electrons/Bohr<sup>3</sup>, respectively [35]. The total variance is defined as:  $\sigma^2 = \sigma_+^2 + \sigma_-^2$ . The enthalpy of sublimation is calculated by Equation 5 [13]:

$$\Delta H_{sub} = aA_{iso}^2 + b(v\sigma^2)^{0.5} + c \quad (5)$$

In Equation 5,  $A_{iso}$ , is defined as the area of the molecular surface of the 0.001 electrons/Bohr<sup>3</sup> isosurface,  $a = 17.728 \times 10^{-4} \text{ \AA}^{-4} \cdot \text{kJ/mol}$ ,  $b = 10.799$  and  $c = -28.192 \text{ kJ/mol}$ . The Multiwfn software was used to calculate  $\sigma_+^2$ ,  $\sigma_-^2$ ,  $v$  and  $A_{iso}$  from geometries optimized with the B3LYP functional and the 6-31G(d) basis set [36, 37].

### 2.3 Crystal density

A simple method for predicting the crystal density,  $\rho_{cr}$ , is by using Equation 6 [14, 15]:

$$\rho_{cr} = \frac{M}{V_{iso}} \quad (6)$$

where  $M$  is the molecular mass and  $V_{iso}$  is defined as the volume inside the 0.001 electrons/Bohr<sup>3</sup> isosurface of the electron density. The crystal density was also calculated with an empirical model based on the ESP parameters [14]:

$$\rho_{cr} = \alpha \left( \frac{M}{V_{iso}} \right) + \beta v \sigma^2 + \gamma \quad (7)$$

where  $\alpha = 1.0462$ ,  $\beta = 1.198 \times 10^{-4} \text{ g}/(\text{cm}^3(\text{kJ}/\text{mol})^2)$ , and  $\gamma = -0.1586 \text{ g}/\text{cm}^3$ . The geometry of the molecule was optimized at the B3LYP/6-31G(d,p) level.

The detonation properties were calculated with EXPLO5 v5.05 software [38]. The input parameters to the EXPLO5 software are the solid density and the energy of formation of the compound in the solid state. The specific impulses for rocket propellants were calculated using the Chemical Equilibrium with Application v.2 software [39]. The chamber pressure was 70 bar and the expansion ratio was 70/1. The quantum chemical calculations were performed by using the DFT or the complete basis set method as implemented in the GAUSSIAN09 software [40].

## 2.4 Impact sensitivity

One of the most frequently used measures of hazard is the impact sensitivity, which is found by dropping a mass, usually 2.5 kg, upon a sample and determining the height,  $H_{50}$ , from which 50% of the drops lead to reaction. Since there is no general formula that predicts the sensitivity accurately for the different classes of energetic materials it is more convenient to look for trends between the impact sensitivity and factors like the heat of detonation, the free space per molecule in the crystal lattice and the bond dissociation energy [41]. Such coarse methods can be useful in order to evaluate if a new molecule will be most probably a high sensitivity or a low sensitivity energetic material. Fried *et al.* examined the relationship between the decomposition energy, the bond dissociation energy of the weakest bond in the molecule, and the impact sensitivity. They reported a fair correlation between bond dissociation energy and impact sensitivity for low-sensitivity explosives. For more sensitive explosives, there was a strong correlation between the decomposition energy and the impact sensitivity [42].

A recent evaluation of the relation between the impact sensitivity and heat of detonation shows that there is a trend between these two factors, but not a correlation [43]. Crystalline properties such as polymorphic form, hardness, compressibility, cracks, defects and voids are important factors for the impact sensitivity of an energetic material. Politzer and Murray showed that there is a trend between the free space per molecule in the crystal lattice and the impact sensitivity [41]. The free space per molecule,  $\Delta V$ , is expressed by Equation 8:

$$\Delta V = V_{eff} - V_{int} \quad (8)$$

where  $V_{eff}$  is the molecular mass divided by the density and  $V_{int}$  is defined as the volume enclosed by the 0.003 electrons/Bohr<sup>3</sup> isosurface of the electron density calculated at the B3PW91/6-31G(d,p) level. The densities predicted with Equation 7 are used to calculate  $V_{eff}$  if no experimental value is available. According to Politzer and Murray, nitramines show little or no correlation between the impact sensitivity and the heat of detonation or the free space per molecule [41, 43]. Hence, there must be other factors which determine the impact sensitivities of nitramines. The dissociation of the N–NO<sub>2</sub> bond is assumed to be the key step in the initiation process [2] and this factor may give an indication of the sensitivity and stability of the derivatives. The bond dissociation energy,  $E_b$ , at T = 0 K of the bond A–NO<sub>2</sub> is:

$$E_b = E(A\cdot) + E(NO_2\cdot) - E(A - NO_2) \quad (9)$$

where  $E(A\cdot)$ ,  $E(NO_2\cdot)$  and  $E(A - NO_2)$  denote the ground state energies (open shell model and zero point energy included) of the species  $A\cdot$ ,  $NO_2\cdot$  and  $A - NO_2$ , respectively. The hybrid DFT functional B3LYP with the 6-31G (d) basis set was used to calculate the bond dissociation energy. This functional is widely used for the computation of optimized structures and thermochemical quantities of energetic materials.

In molecules which are rich in nitro groups, the geometries as well as the energies have been erroneously calculated by the B3LYP functional [44]. Compared to experimental data this functional also underestimated the C–N bond dissociation energy by 23.4 kJ/mol on average [45]. Therefore, the bond dissociation energies were calculated with another hybrid DFT functional, M06-2X, which has been reported to calculate the bond dissociation energies more accurately than B3LYP [46]. The B3LYP and M06-2X functionals contain a number of constants that are fitted to experimental data and the calculated geometries and energies will therefore depend to some extent on the



parameterization set. Therefore, a non-DFT method was also used to calculate the bond dissociation energy. This method, CBS-4M, is based on the Hartree-Fock theory and the Møller-Plesset perturbation theory.

Keshavarz developed a general equation for calculating the impact sensitivity based on the stoichiometric molecular formula  $C_aH_bN_cO_d$  with contributions from specific functional groups and structures. Equation 10 is based on a number of different classes of energetic compounds, including nitrotriazoles and nitramines.

$$\log H_{50} = -0.584 + 61.62a' + 21.53b' + 27.96c' + (84.47 F^+ / MW) - (147 F^- / MW) \quad (10)$$

where  $a'$ ,  $b'$  and  $c'$  are the numbers of C, H and N atoms, respectively, divided by the molecular mass (MW) of the energetic compound. The constants  $F^+$  and  $F^-$  are dependent upon the molecular structure in the energetic molecule and their values are specified in ref. [47]. The root mean square of deviation for Equation 10 was reported to be 5.9 J.

### 3 Results

The molecular structures were first geometry optimized with the B3LYP/6-31G (d,p) functional. The optimized structures showed that the NTO and ANTA derivatives had a planar conformation when no nitro groups were present at neighbouring positions in the molecule. Otherwise, the nitro groups were twisted out of the plane. None of the optimized geometries had imaginary frequencies, indicating that these geometries were at least local minimums of the potential energy surface.

#### 3.1 Crystal density and enthalpy of formation

Table 1 shows a comparison of the two models used to calculate the crystal density. Some experimental values are also included in the table. It can be seen that Equations 6 and 7 give reasonably good approximations, but both methods significantly underestimate the density of NTO and 1,3,4-trinitro-1,2,4-triazol-5-one. The densities predicted with Equation 7 were used as input parameters in the calculation of the detonation properties. Table 1 also displays the enthalpy of formation of the solid for the various energetic compounds. The calculated values for RDX, TNT, NTO and ANTA are in good agreement with experimental results. From Table 1 it is observed that the enthalpy of formation increases with the number of nitro groups substituted onto ANTA and NTO.

**Table 1.** Calculated and experimental densities and enthalpies for RDX, TNT, ANTA, NTO and the derivatives

Compound	Density [g/cm <sup>3</sup> ]			Enthalpy [kJ/mol]			
	Eq. (6)	Eq. (7)	Exp.	$\Delta H_{\text{sub}}$	$\Delta H_f(\text{g})$	$\Delta H_f(\text{s})$	$\Delta H_f^{\text{exp}}(\text{s})$
RDX	1.797	1.783	1.82 <sup>a</sup>	102.1	176.1	74	70.3 <sup>c</sup>
TNT	1.709	1.673	1.65 <sup>a</sup>	103.6	11.1	-92.5	-80.5 <sup>c</sup>
NTO	1.781	1.797	1.91 <sup>a</sup>	76.1	-16.6	-92.7	-100.8 <sup>a</sup>
1,3-dinitro-1,2,4-triazol-5-one	1.918	1.914		80.3	98.7	18.4	
2,3-dinitro-1,2,4-triazol-5-one	1.907	1.912		84.1	184.8	100.7	
3,4-dinitro-1,2,4-triazol-5-one	1.922	1.907		76.7	126.7	50	
1,3,4-trinitro-1,2,4-triazol-5-one	2.009	1.982	2.07 <sup>b</sup>	82.7	246	163.3	
ANTA	1.678	1.791	1.82 <sup>c</sup>	111.6	188.7	77.1	87.8 <sup>c</sup>
5-amino-1,3-dinitro-1,2,4-triazole	1.844	1.889		102.8	279.6	176.8	
5-amino-3,4-dinitro-1,2,4-triazole	1.846	1.887		99.7	313.3	213.6	
5-nitramino-3-nitro-1,2,4-triazole	1.843	1.891	1.94 <sup>d</sup>	97.5	249.7	152.1	
5-nitrimino-3-nitro-1,2,4-triazole	1.851	1.894		102.6	272.4	169.7	

Ref. [<sup>a</sup> 48, <sup>b</sup> 4, <sup>c</sup> 49, <sup>d</sup> 5, <sup>e</sup> 50]

### 3.2 Detonation and propellant properties

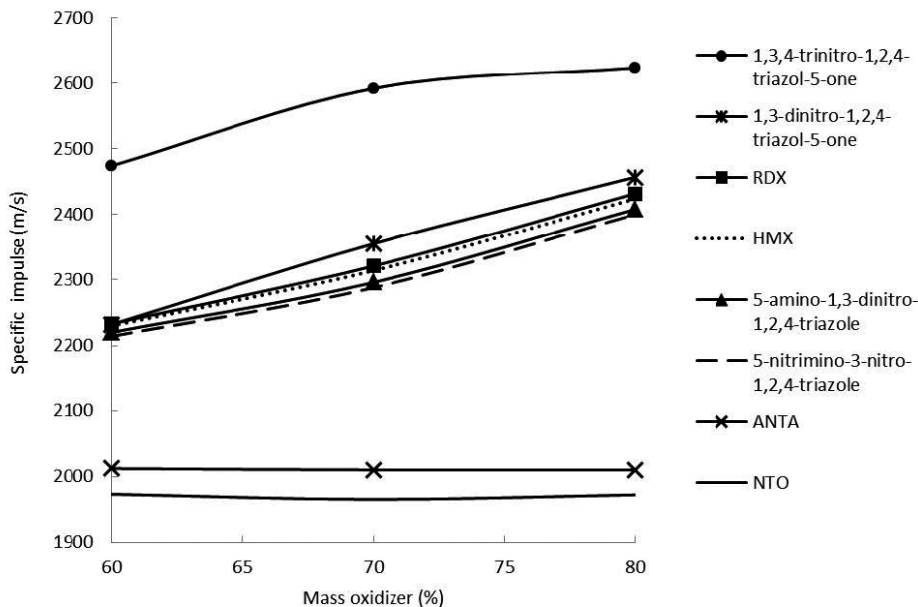
The detonation properties are listed in Table 2. The results show that if one nitro group is substituted onto NTO or ANTA, the detonation velocity and pressure will be at nearly the same level or slightly higher than in the case of RDX. The oxygen balance increased to 4.6% for the mono-nitrated NTO compounds and to -9.2% for the corresponding ANTA derivatives. In addition, the detonation temperature increased by approximately 1000 K when one nitro group was substituted. If two nitro groups were substituted onto NTO, the detonation velocity and pressure were reduced compared to RDX, but the oxygen balance increased to 21.8% and the detonation temperature increased by more than 600 K. However, none of the derivatives has better detonation properties than HMX. Figure 2 shows the specific impulse for the various compounds in compositions with GAP. It can be seen that if one nitro group is substituted onto NTO, the impulses are somewhat higher than that of RDX. When two nitro groups are substituted onto NTO, an impulse just above 2600 m/s is achieved, which is at the same level as

ammonium dinitramide (ADN) in a GAP matrix. The ANTA derivatives show similar trends as NTO when one nitro group is substituted onto the molecule.

**Table 2.** Calculated heat of detonation (Q), detonation pressure (P), detonation velocity (D), temperature of detonation ( $T_{\text{ex}}$ ), volume of the gaseous detonation products (V), and oxygen balance

Compound	Q [kJ/kg]	P [kbar]	D [m/s]	$T_{\text{ex}}$ [K]	V [L/kg]	Oxygen balance [%]
HMX <sup>a</sup>	6050	400	9145	4114	730	-21.6
RDX	6141	345	8735	4224	740	-21.6
TNT	5097	218	7265	3592	574	-74.0
NTO	4141	267	7883	3387	685	-24.6
1,3-dinitro-1,2,4-triazol-5-one	5280	350	8641	4386	671	4.6
2,3-dinitro-1,2,4-triazol-5-one	5703	366	8792	4675	671	4.6
3,4-dinitro-1,2,4-triazol-5-one	5445	354	8680	4491	671	4.6
1,3,4-trinitro-1,2,4-triazol-5-one	4371	330	8389	4023	662	21.8
ANTA	4194	276	8181	3227	736	-43.4
5-amino-1,3-dinitro-1,2,4-triazole	5742	366	8839	4452	701	-9.2
5-amino-3,4-dinitro-1,2,4-triazole	5944	379	8987	4549	699	-9.2
5-nitramino-3-nitro-1,2,4-triazole	5605	367	8878	4360	700	-9.2
5-nitrimino-3-nitro-1,2,4-triazole	5704	373	8927	4409	700	-9.2

<sup>a</sup>  $\Delta H_f(s)$  from EXPLO5-database



**Figure 2.** Calculated specific impulse for ANTA, HMX, NTO, RDX and the derivatives in compositions with the energetic polymer GAP.

### 3.3 Impact sensitivity

A high sensitivity secondary explosive tends to have a high heat of detonation, while a low sensitivity secondary explosive is likely to have a small heat of detonation. Table 2 illustrates this trend where the low sensitivity compounds ANTA and NTO have the smallest heats of detonation. The other derivatives, except 1,3,4-trinitro-1,2,4-triazol-5-one, have heat of detonation values comparable to RDX, which indicates that the derivatives could be considered as rather sensitive nitramines. The low heat of detonation for 1,3,4-trinitro-1,2,4-triazol-5-one showed that this compound might have a lower sensitivity than TNT, which is consistent with experimental findings.

Table 3 displays the free space per molecule in the crystal lattice and also the measured impact sensitivities. ANTA and NTO, which have the lowest sensitivities, have also the smallest calculated free space per molecule. All of the derivatives have a free space per molecule smaller than that of RDX. 5-Nitrimino-3-nitro-1,2,4-triazole has a measured impact sensitivity of 1 J, while the free space was calculated to be  $29.1 \text{ \AA}^3$ . By comparison, the free space of 1,3,4-trinitro-1,2,4-triazol-5-one was  $36.3 \text{ \AA}^3$  while its measured impact

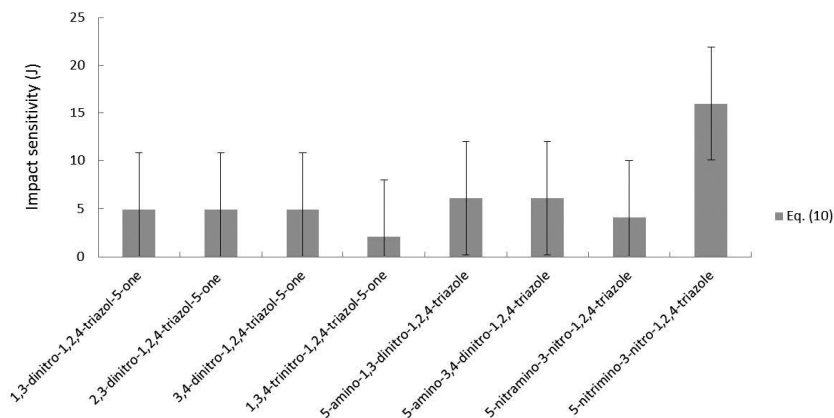
sensitivity was 24 J. Thus, the value of 5-nitramino-3-nitro-1,2,4-triazole is an outlier compared to the general trend where low free space indicates low sensitivity. However, the impact sensitivities for nitramines show only a weak trend with the free space per molecule in the crystal lattice [41].

**Table 3.** The molecular mass, the density,  $V_{\text{eff}}$ ,  $V(0.003)$ ,  $\Delta V$  and the measured impact sensitivities for RDX, TNT, NTO, ANTA and the derivatives

Compound	M [g/mol]	$\rho$ [g/cm <sup>3</sup> ]	$V_{\text{eff}}$ [Å <sup>3</sup> ]	$V(0.003)$ [Å <sup>3</sup> ]	$\Delta V$ [Å <sup>3</sup> ]	Impact sensi- tivity [J]
RDX	222.1	1.81 <sup>a</sup>	203.8	158.4	45.4	7.5 <sup>a</sup>
TNT	227.1	1.65 <sup>a</sup>	228.6	169.6	59.0	15 <sup>a</sup>
NTO	130.1	1.91 <sup>a</sup>	113.1	91.6	21.5	71 <sup>c</sup>
1,3-dinitro-1,2,4-triazol-5-one	175.1	1.914	151.9	115.6	36.3	
2,3-dinitro-1,2,4-triazol-5-one	175.1	1.912	152.0	116.4	35.6	
3,4-dinitro-1,2,4-triazol-5-one	175.1	1.907	152.4	116.6	35.8	
1,3,4-trinitro-1,2,4-triazol-5-one	220.1	2.07 <sup>b</sup>	176.6	140.2	36.3	24 <sup>b</sup>
ANTA	129.1	1.82 <sup>c</sup>	117.8	95.5	22.3	100 <sup>c</sup>
5-amino-1,3-dinitro-1,2,4-triazole	174.1	1.889	153.0	120.8	32.2	
5-amino-3,4-dinitro-1,2,4-triazole	174.1	1.887	153.2	118.7	34.5	
5-nitramino-3-nitro-1,2,4-triazole	174.1	1.94 <sup>d</sup>	149.0	119.9	29.1	1 <sup>d</sup>
5-nitrimino-3-nitro-1,2,4-triazole	174.1	1.894	152.6	118.8	33.8	

Ref. [<sup>a</sup>48, <sup>b</sup>4, <sup>c</sup>49, <sup>d</sup>5]

The impact sensitivities have been calculated using Equation 10 and are displayed in Figure 3. If the root mean square deviation in Equation 10 is taken into account, Figure 3 shows that the derivatives tend to be rather impact sensitive. The exception was the impact sensitivity of 5-nitrimino-3-nitro-1,2,4-triazole, which was estimated by Equation 10 to be 16 J.



**Figure 3.** Calculated impact sensitivities (J) for the derivatives. The error bars are the root mean square of deviation (5.9 J) from ref. [47].

### 3.4 Stability

From Table 1 it can be seen that when  $\text{NO}_2$  is substituted onto NTO, the enthalpy of formation is increased and is dependent on which nitrogen position the  $\text{NO}_2$  group is substituted. The largest increase in enthalpy of formation occurred when  $\text{NO}_2$  was substituted on the nitrogen at position 2 in 1,2,4-triazol-5-one. The lowest increase in enthalpy of formation occurred when  $\text{NO}_2$  was substituted at the nitrogen atom in position 1. Subsequently, the thermodynamic stability of NTO with one  $\text{NO}_2$  group substituted can be ranked as follows: 1,3-dinitro-1,2,4-triazol-5-one > 3,4-dinitro-1,2,4-triazol-5-one > 2,3-dinitro-1,2,4-triazol-5-one. When two  $\text{NO}_2$  groups were substituted onto NTO, the enthalpy of formation increased to 256 kJ/mol. The same trend was seen when a  $\text{NO}_2$  group was substituted onto ANTA, but in this case the enthalpy of formation increased slightly less. This was especially true when the  $\text{NO}_2$  group was substituted onto the  $\text{NH}_2$  group and formed a nitramine ( $\text{NH}-\text{NO}_2$ ) or a nitrimino ( $\text{C}=\text{N}-\text{NO}_2$ ) group. 5-Nitramino-3-nitro-1,2,4-triazole had the lowest increase in the enthalpy of formation, while the largest increase was found for 5-amino-3,4-dinitro-1,2,4-triazole. As shown in Table 1, the thermodynamic stability of the ANTA derivatives with one substituted  $\text{NO}_2$  group can be ordered as follows: 5-nitramino-3-nitro-1,2,4-triazole > 5-nitrimino-3-nitro-1,2,4-triazole > 5-amino-1,3-dinitro-1,2,4-triazole > 5-amino-3,4-dinitro-1,2,4-triazole.

All of the derivatives have one or two  $\pi$  bonds in the 1,2,4-triazole ring. The carbon atom in the 5-position is either bound to an electron donating  $\text{NH}_2$  group or has a  $\pi$  bond to a nitrogen or an oxygen atom. These  $\pi$  bonds and the

NH<sub>2</sub> group may enhance structural resonance, which stabilizes the molecule. However, substitution of an electron withdrawing NO<sub>2</sub> group will pull electrons out of the ring and reduce the resonance stabilization. This effect is illustrated by the fact that several bonds in the 1,2,4-triazole increased in length when two NO<sub>2</sub> groups were substituted onto NTO. For instance, the length of the N4–C5 bond increased from 1.404 to 1.440 Å when NO<sub>2</sub> was substituted onto the nitrogen in positions 2 and 4, respectively.

Table 4 shows the N–NO<sub>2</sub> bond dissociation energy calculated by the M06-2X/6-31G(d) functional for the weakest bond in the derivatives. The bond dissociation energies were between 43 and 134 kJ/mol, depending on the position of the nitro group in NTO. 1,3,4-trinitro-1,2,4-triazol-5-one has weak N–NO<sub>2</sub> bonds even though the impact sensitivity is measured to be 24 J [4]. Weak N–NO<sub>2</sub> bonds are also seen in the ANTA derivatives where the lowest bond dissociation energy was calculated to be 70 kJ/mol. In general, the N–NO<sub>2</sub> bonds in the derivatives were weaker than the N–NO<sub>2</sub> bonds in RDX, except for the N–NO<sub>2</sub> bond in the nitrimino group. The N–NO<sub>2</sub> bond dissociation energy of the nitrimino group was calculated to be around 300 kJ/mol, which is considerably higher than the N–NO<sub>2</sub> bond dissociation energy in RDX. The bond dissociation energies of C–NO<sub>2</sub> were significantly higher than for N–NO<sub>2</sub>. The C–NO<sub>2</sub> bond in the NTO derivatives was weakened when at least one further nitro group was substituted onto a nitrogen in 1,2,4-triazole. The same effect was seen in the ANTA derivatives, except for when a nitro group was substituted onto the NH<sub>2</sub> group. In that case, the C–NO<sub>2</sub> bond dissociation energy was changed only slightly.

**Table 4.** The N–NO<sub>2</sub> bond dissociation energies (kJ/mol) calculated by the functional M06-2X/6-31G(d) for the weakest bond in the derivatives

Compound	Bond	E <sub>b</sub> [kJ/mol]
1,3-dinitro-1,2,4-triazol-5-one	N1–NO <sub>2</sub>	134
2,3-dinitro-1,2,4-triazol-5-one	N2–NO <sub>2</sub>	43
3,4-dinitro-1,2,4-triazol-5-one	N4–NO <sub>2</sub>	86
1,3,4-trinitro-1,2,4-triazol-5-one	N4–NO <sub>2</sub>	94
5-amino-1,3-dinitro-1,2,4-triazole	N1–NO <sub>2</sub>	135
5-amino-3,4-dinitro-1,2,4-triazole	N4–NO <sub>2</sub>	70
5-nitramino-3-nitro-1,2,4-triazole	N6–NO <sub>2</sub>	161
5-nitrimino-3-nitro-1,2,4-triazole	N6–NO <sub>2</sub>	305

If we examine the relationship between the two different DFT functionals and the CBS-4M method, some differences in the calculated bond dissociation

energies are seen. The B3LYP/6-31G(d) method gives a bond dissociation energy that is on average 34 kJ/mol lower than that calculated by the CBS-4M method. However, the bond dissociation energy for the derivative with the nitrimino functional group differs. The difference is relatively large, being 106 kJ/mol lower when the B3LYP functional is used. The bond dissociation energies calculated with the CBS-4M method and the M06-2X/6-311G+(2d,p) functional deviated by 3 kJ/mol on average. By using M06-2X with the larger basis set 6-311+G(2d,p), the bond dissociation energies for the derivatives decreased by 8 kJ/mol on average compared to the values obtained with the 6-31G(d) basis set with the M06-2X functional.

The thermal stability and compatibility of the derivatives could limit their applicability as energetic materials. Melting and decomposition temperatures below 200 °C have been measured for triazoles with N-bonded NO<sub>2</sub>, and nitrourea-like compounds such as 1,3,4-trinitro-1,2,4-triazol-5-one may have compatibility problems [5, 51]. Several di-nitrourea compounds are easily hydrolyzed, while mono-nitroureas have better water stability. The temperature stability of di-nitrourea compounds varies. For instance, N,N'-dinitrourea (DNU) decomposes at 130 °C, while thermogravimetric analysis (TGA) showed that 1,3,4-trinitro-1,2,4-triazol-5-one was stable up to 194 °C [4, 52].

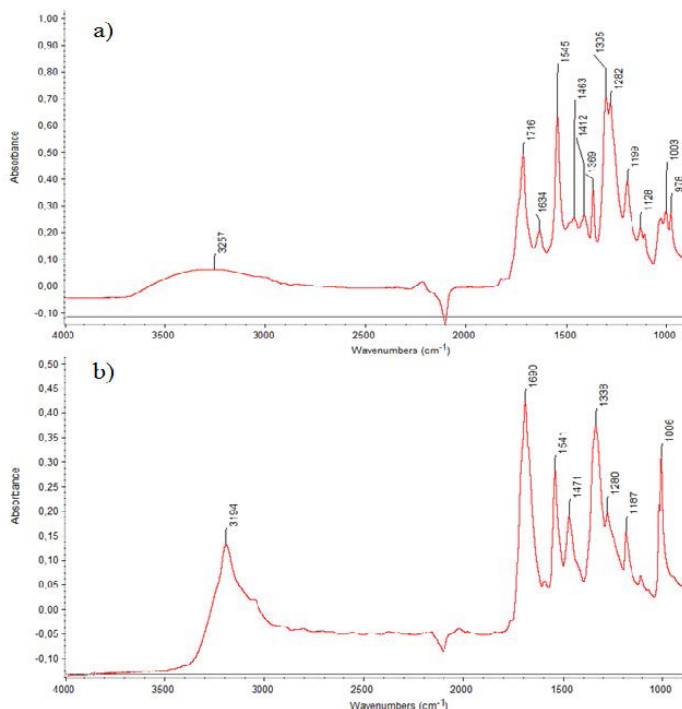
The compatibility of 1,3,4-trinitro-1,2,4-triazol-5-one is not reported in the literature, but the low N-NO<sub>2</sub> bond dissociation energy may indicate that the compatibility might be poor. However, the reaction mixture with 1,3,4-trinitro-1,2,4-triazol-5-one was poured over crushed ice and then filtered at the end of the synthesis of this compound [4]. Thus, the derivative must tolerate some contact with water without being hydrolysed. If the derivatives follow the same trend as the mono- and dinitro-urea compounds, 1,3-dinitro-1,2,4-triazol-5-one will probably be more compatible with water than 1,3,4-trinitro-1,2,4-triazol-5-one. Dippold *et al.* measured the decomposition temperature for 5-nitramino-3-nitro-1,2,4-triazole to be 135 °C [5]. If the nitramino functional group in 5-nitramino-3-nitro-1,2,4-triazole is changed into a nitrimino functional group, the N-NO<sub>2</sub> bond dissociation energy increases from 161 to 305 kJ/mol. This may indicate that 5-nitrimino-3-nitro-1,2,4-triazole could be more thermally stable than 5-nitramino-3-nitro-1,2,4-triazole.

### 3.5 Synthesis

We investigated whether zinc chloride, ammonium chloride or sodium chloride could replace hydrochloric acid in the chloride-assisted nitrolysis of NTO. Sodium chloride was poorly soluble in acetic anhydride and nitric acid at 0 °C. Therefore, the nitration was carried out using zinc chloride or ammonium chloride



together with acetic anhydride and nitric acid. The synthetic route reported by Jadhav [4] was tried out first, except that hydrochloric acid was replaced by zinc chloride. When the mixture was kept at 40 °C for 1-2 hours with excess nitric acid, the Fourier transform infrared (FTIR) spectrum of the product showed that there was no carbonyl left. Consequently, the product could not be 1,3,4-trinitro-1,2,4-triazol-5-one or any other nitrourea.



**Figure 4.** FTIR spectra (ATR) of (a) an NTO derivative and (b) NTO.

When the stoichiometric ratio between NTO and nitric acid was used at temperatures below 15 °C, the carbonyl band in the FTIR spectrum was shifted towards a higher wavenumber (1716  $\text{cm}^{-1}$ ), which is consistent with the calculated FTIR spectrum (M06-2X/6-31G(d)) of NTO and 1,3-dinitro-1,2,4-triazol-5-one. The intensity of the N-H (stretching) absorption band (3194  $\text{cm}^{-1}$ ) was also significantly reduced – see Figure 4. The absorption band at 1545  $\text{cm}^{-1}$  increased in intensity compared to the absorption band of NTO at 1541  $\text{cm}^{-1}$ . The band at 1545  $\text{cm}^{-1}$  represents the nitro group. The calculated FTIR spectrum of 1,3-dinitro-1,2,4-triazol-5-one indicated that there could also be an N-NO<sub>2</sub>

absorption band between the carbonyl ( $1716\text{ cm}^{-1}$ ) and the nitro ( $1545\text{ cm}^{-1}$ ) bands. Indeed, a band did appear at  $1634\text{ cm}^{-1}$  which is a high wavenumber for an N–NO<sub>2</sub> bond, but it should be borne in mind that the wavenumber correlates with the N–NO<sub>2</sub> bond length [53]. The calculated N–NO<sub>2</sub> bond length of 1,3-dinitro-1,2,4-triazol-5-one is  $1.450\text{ Å}$ , which is a relatively long N–NO<sub>2</sub> bond. In summary, these facts indicated that new N–NO<sub>2</sub> bonds have been formed.

A mixture with similar stoichiometry and reaction conditions, but without zinc chloride, was also prepared. NTO decomposed completely in this mixture and no product was recovered, neither by filtration nor evaporation. When ammonium chloride was used together with nitric acid and acetic anhydride, the FTIR analyses showed that only NTO was recovered. Thus, zinc chloride seemed to be a more potent chloride source than ammonium chloride in the chloride-assisted nitrolysis of NTO. It should be noted that the derivative obtained was unstable. After 24 h at room temperature the derivative had decomposed. When the derivative was washed with cold acetone in addition to chloroform, the stability was not improved.

## 4 Conclusion

Incorporation of nitrated ANTA and NTO derivatives in rocket propellants showed a significant improvement in the specific impulse. If one nitro group was substituted onto ANTA or NTO, the performance reached the same level as RDX propellants. By substituting two nitro groups onto NTO, impulses above  $2600\text{ m/s}$  were obtained if a GAP matrix was used as binder. The detonation properties of the derivatives calculated with the EXPLO5 software were comparable to or slightly better than RDX. The heats of detonation and the CHNO-ratios were applied to evaluate the impact sensitivities, and the results showed that the derivatives could be characterized as rather sensitive nitramines. Bond dissociation energies were calculated with the DFT functionals B3LYP and M06-2X. The non-DFT method CBS-4M was also used. The calculations showed that the N–NO<sub>2</sub> bonds could be weak, with bond energies from 41 to 296 kJ/mol when calculated at the M06-2X/6-311+G(2d,p) level. The low N–NO<sub>2</sub> bond dissociation energy in the derivatives indicated that they might have poor stability and sensitivity. The N–NO<sub>2</sub> bond in the nitrimino functional group has a bond dissociation energy as high as 296 kJ/mol. Therefore, 5-nitrimino-3-nitro-1,2,4-triazole may have tolerable stability and sensitivity, making this derivative a candidate for synthesis. Based on the reported synthesis of 1,3,4-trinitro-1,2,4-triazol-5-one, 5-nitramino-3-nitro-1,2,4-triazole and 5-nitriminotetrazole, synthetic routes for

5-nitrimino-3-nitro-1,2,4-triazole, 1,3-dinitro-1,2,4-triazol-5-one and 3,4-dinitro-1,2,4-triazol-5-one were suggested. When NTO was dissolved in a mixture of nitric acid and acetic anhydride the compound decomposed. NTO did not seem to decompose if chloride-assisted nitration was used and the temperature was kept below 15 °C. The FTIR spectrum of a derivative obtained indicated that an N–NO<sub>2</sub> bond had been formed in the molecule. However, the derivative was not stable for more than 24 h at room temperature.

## 5 Experimental Section

NTO was used as received from Chemring Nobel. Sigma-Aldrich supplied acetic anhydride and concentrated nitric acid. The FTIR spectra were recorded on a Nicolet FTIR (iS10) with diamond ATR. The absorbance bands were characterized as broad (b), strong (s), medium (m) and weak (w).

### 5.1 Nitration of NTO in the presence of zinc chloride

Acetic anhydride (1.86 g) was added dropwise to nitric acid (0.69 g) at 0 °C. The solution was stirred for 30 min before zinc chloride (0.15 g) was dissolved in the mixture. After stirring for 30 min, small portions of NTO (0.30 g) were added. This mixture was stirred for 1 h, heated to 15–18 °C and stirred overnight. Finally, it was heated to 40 °C and stirred for 2 h. During the reaction the colour of the slurry-like mixture changed from yellow to weak-red and then to white. The slurry was poured into a beaker containing ice-cold water and the precipitate was filtered off and washed with water. The precipitate dissolved rapidly and decomposed during the washing step. The procedure was repeated using chloroform instead of water. The precipitate was more stable in this solvent and was therefore filtered off and dried under vacuum. IR (ATR):  $\tilde{\nu}$  = 3363 (b), 2215 (w), 1542 (s), 1455(s), 1408 (s), 1301(s), 1028 (m), 957 (w), 809 (w) cm<sup>-1</sup>.

Acetic anhydride (1.57 g) was added dropwise to nitric acid (0.57 g) at 0 °C. After 30 min stirring, zinc chloride (0.27 g) was dissolved in the mixture, followed by stirring for 30 min. After addition of NTO (0.59 g) in small portions, the mixture was stirred for 1 h, then heated to 15 °C and stirred overnight. Thereafter, the white slurry was poured into cold chloroform and filtered off. The precipitate was dried under vacuum, washed with acetone, filtered and dried. FTIR (ATR):  $\tilde{\nu}$  = 3207 (b), 1717 (m), 1639 (w), 1546 (s), 1456 (m), 1411 (m), 1369 (m), 1290 (s), 1108 (w), 1022 (m), 977 (m), 861 (w) cm<sup>-1</sup>.

Nitric acid (0.36 g) was cooled to 0 °C and acetic anhydride (2.06 g) was then added dropwise. The mixture was stirred for 20 min before zinc chloride

(0.20 g) was added followed by stirring for 30 min at 0 °C. Subsequently, small portions of NTO (0.38 g) were added and the mixture was stirred for 5 h at 0-5 °C, poured into cold chloroform (5.0 g), filtered off, washed with chloroform (10.0 g) and dried under vacuum. The product consisted of small white crystals. FTIR (ATR):  $\tilde{\nu}$  = 3257 (b), 1716 (s), 1634 (w), 1545 (s), 1463 (w), 1412 (w), 1369 (m), 1305 (s), 1282 (s), 1199 (m), 1128 (w), 1003 (m), 978 (m)  $\text{cm}^{-1}$ .

## 5.2 Nitration of NTO in the presence of ammonium chloride

Acetic anhydride was dripped into nitric acid at 0 °C. After stirring for 30 min, ammonium chloride was added. The mixture was stirred for 30 min before the addition of small portions of NTO, followed by stirring for 1 h. The mixture was then heated, first to room temperature and stirred for 4 h, then to 35-40 °C and stirred for 1 h. The white slurry was poured onto crushed ice, filtered off and dried. FTIR (ATR):  $\tilde{\nu}$  = 3194 (m), 1690 (s), 1539 (m), 1471 (m), 1338 (s), 1279 (m), 1186 (m), 1108 (w), 1005 (m)  $\text{cm}^{-1}$ .

FTIR spectrum of NTO (ATR):  $\tilde{\nu}$  = 3194 (m), 1690 (s), 1541 (m), 1471 (m), 1338 (s), 1280 (m), 1187 (m), 1109 (w), 1006 (m)  $\text{cm}^{-1}$ .

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