Received: 6 March 2023 | Revised: 26 April 2023 | Accepted: 27 April 2023

DOI: 10.1002/prep.202300062

Propellants, Explosives, Pyrotechnics

RESEARCH ARTICLE

Investigation of a new promising process for the RDX synthesis *via* 1,3,5-triacetyl-1,3,5-triazinane (TRAT)

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Dedicated to Professor Jean'ne M. Shreeve on Occasion of her 90th Birthday.

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Funding information
Ludwig Maximilian University (LMU); EMTO GmbH; BIAZZI SA

Abstract

Despite intensive research for possible replacements, RDX (1,3,5-trinitro-1,3,5-triazinane) is still considered to be one of the most important energetic materials because of its versatile application. Due to the high demand for RDX, optimization of synthesis and development of new methods are of great interest to both academia and industry. Therefore, in this work, the synthesis of RDX *via* the intermediate TRAT (1,3,5-triacetycl-1,3,5-triazinane) was investigated as a possible alternative industrial production method. In addition to the synthesis of TRAT starting from 1,3,5 trioxane, various feasible nitration methods from TRAT to RDX were investigated. Moreover, the suitability for large-scale production, the comparison of already established methods and the feasibility of a new flow process were discussed.

KEYWORDS
energetic materials, hexogen, industrial production, octogen, synthesis

1 | INTRODUCTION

In the context of its main application as military explosive, it is surprising that RDX was developed and patented as a urinary antiseptic. In 1899, Henning first synthesized RDX by the reaction of nitric acid with the previously known urinary antiseptic hexamine [1]. Its explosive properties and structure were not recognized until more than two decades later and arouse the interest of the military research establishments of several nations in the 1930s. With the start of World War II research in its production proliferated and the compound received various trivial names [2]. In the United Kingdom it was referred to as RDX, in the USA as cyclonite, in Germany as Hexogen and in Italy as T4 [3,4]. Documentation reveals, that in 1941 the British began the large-scale production of RDX to meet the demand for a more powerful explosive than TNT (2,4,6-trinitrotoluene) on the battlefield [5]. For this the Woolwich method was applied, which is based on the treatment of hexamine with concentrated nitric acid [6]. Later that year, the USA started the industrial production utilizing the same method and proceeded the research in more efficient methods [5]. The following year, the Bachmann process was introduced, substantially reducing the required nitric acid and increasing the quantity of produced RDX content [7,8]. Through this synthesis route the higher homologue 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (high melting explosive, HMX) was first received [3,9]. The Bachmann process, in contrast to the Woolwich process, always yields a mixture of RDX with up to 19% of HMX [10,11]. Octogen (HMX) exhibits a

higher density, melting point and detonation performance than Hexogen (RDX) [12]. However, due to its lower production cost, RDX is used predominantly. With regard to the global RDX market, its market size value in 2021 was reported to be 12.1 billion USD and it is predicted to reach 15.4 billion USD by 2030 [13]. The RDX market can be segmented among others by application or by type of use as shown in Figure 1 [14].

The areas of application are divided into the civilian and military sectors, whereby the military sector dominates with a proportion of approximately 80% [13,14]. In the civil sector, RDX is mainly used in the construction and mining industries [13,14]. Whereas in the military sector RDX is used for various applications, e.g. in its phlegmatized form in war heads and bombs or in propellant formulations (e.g. EX-99) [3,15,16]. Moreover, to reduce the risk of accidental detonation, RDX is often used in combination with a binder in plastic-bonded explosives (PBX) or with TNT as a less sensitive explosive, in an effort to desensitize the explosive charge. Examples of such explosive formulations are Composition A (RDX/Wax), Composition B (RDX/TNT/Wax) or the popular formulation Composition C4 (RDX/polyisobutylene) [3]. Dividing the RDX market by type of use, it can be split into explosives, fireworks and others [17]. However, all these sectors are ongoingly increasing due to the growth of the defence, industrial and construction industries [13,14].

Due to the high demand of RDX, synthesis optimization and the development of novel methods are of great interest by the scientific community and industry. Nowadays, there are various synthesis routes towards RDX known, [18,19] Figure 2 shows the Bachmann and the Woolwich process, which are still used for industrial RDX synthesis in a continuous process with CSTR (continuous-stirred tank reactor) [20] systems.

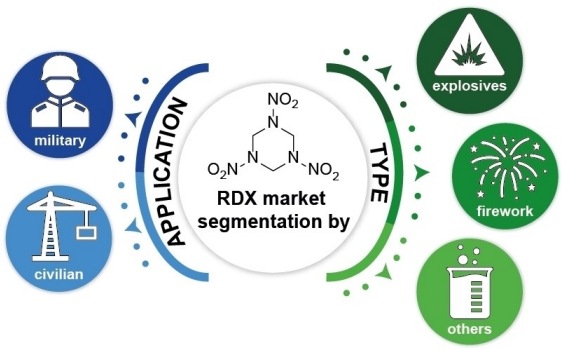


FIGURE 1 Different ways of RDX market segmentation.

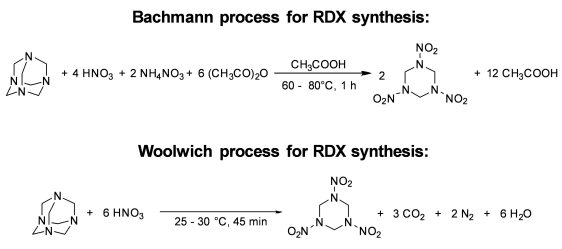


FIGURE 2 Industrial used processes for RDX synthesis.

In this work, the synthesis of RDX *via* the intermediate TRAT (1,3,5-triacetycl-1,3,5-triazinane) was investigated as a possible alternative industrial production method. This is of particular interest since in the literature this reaction pathway has been proposed as a continuous flow synthesis [21]. Due to the advantages in terms of safety and efficiency, the use of a continuous processes for the potential production of HEDMs (high energy dense material) is always preferable and therefore this possible new process attracted considerable interest in academia and industry [20,22].

2 | EXPERIMENTAL SECTION

All chemicals and solvents were employed as received. ^{1}H NMR spectra were recorded with neat solids as samples at ambient temperature using a Bruker TR 400 instrument. The chemical shifts quoted in ppm in the text refer to typical standards such as tetramethylsilane (^{1}H). All NMR spectra were analyzed with the software Mestrenova from Mestrelab Research S. L. Atom labelling and nomenclature are not in correspondence with IUPAC.

CAUTION! All investigated compounds and mixtures are potentially explosive energetic materials, which show partly increased sensitivities towards various stimuli (e.g. elevated temperatures, impact, friction, or electrostatic discharge). Therefore, proper security precautions (safety glass, face shield, earthed equipment and shoes, leather coat, Kevlar gloves, Kevlar sleeves, and ear plugs) have to be applied while synthesizing and handling the described compounds.

2.1 | Synthesis of 1,3,5-Triacetycl-1,3,5-triazinane (TRAT)

TRAT was synthesized according to a modified literature procedure [23]. Ten drops of conc. sulphuric acid where added to acetonitrile (7.90 mL) and the mixture was heated to 50 °C. Trioxane (2.70 g, 30.0 mmol) was added slowly to the warm reaction mixture. Following 30 s of stirring, when a precipitate was visible, the reaction was rapidly cooled down with an ice bath mixed with NaCl. The reaction mixture was stirred for 30 min at 0 °C and NaOH (2 M, 5.00 mL) was added resulting in a large

amount of colourless precipitate. The precipitate was isolated by filtration and was washed with ethyl acetate (100 mL). 1,3,5-Triacetycl-1,3,5-triazinane (3.20 g, 15.0 mmol, 50%) was obtained as a colourless solid.

1,3,5-Triacetyl-1,3,5-triazinane (TRAT)

^{1}H NMR (400 MHz, DMSO-D_6, ppm) δ = 5.21 (s, 6H, −CH_2−), 2.12 (s, 9H, −CH_3).

1,3,5,7-Tetraacetyl-1,3,5,7-tetrazocinane (TAT)

^{1}H NMR (400 MHz, DMSO-D_6, ppm) δ = 4.99 (s, 8H, −CH_2−), 2.14 (s, 12H, −CH_3).

2.2 | Nitration attempts

Nitration of TRAT with HNO_3

TRAT (250 mg, 1.17 mmol) was added gradually while ice cooling to fuming nitric acid (15 mL, 360 mmol, 300 eq.). Following the complete addition, the ice bath was removed and stirred for 1 h at room temperature. The nitration mixture was then quenched on ice. No precipitation was observed and no product was obtained.

Nitration of TRAT with mixed acid (H_2SO_4/HNO_3)

Fuming nitric acid (9 mL, 215 mmol) was added gradually to concentrated sulfuric acid (6 mL, 112 mmol) while ice cooling. TRAT (250 mg, 1.17 mmol) was added slowly under cooling. Following the complete addition, the ice bath was removed and stirred for 1 h at room temperature. The nitration mixture was then quenched on ice. No precipitation was observed and no product was obtained.

Nitration of TRAT with N_2O_5

N_2O_5 (380 mg, 3.51 mmol, 3.00 eq.) was weighted under nitrogen and immediately dissolved in MeCN (10 mL). Parallel TRAT (250 mg, 1.17 mmol) was predissolved in MeCN (10 mL) and added under cooling. Following the complete addition, the ice bath was removed. The reaction mixture was stirred for 1 h at room temperature, poured into a crystallization dish and allowed to evaporate overnight. A mixture of RDX and DANT as colorless oil was obtained.

1,3,5-Trinitro-1,3,5–triazinane (RDX)

^{1}H NMR (400 MHz, DMSO-D_6, ppm) δ = 6.14 (s, 6H, −CH_2−).

1,3-Diacetyl-5-nitro-1,3,5-triazinane (DANT)

^{1}H NMR (400 MHz, DMSO-D_6, ppm) δ = 5.64 (s, 4H, −CH_2−), 5.22 (s, 2H, −CH_2−), 2.12 (s, 6H, −CH_3).

Nitration of TRAT with TFAA & HNO_3

TRAT (1.4 g, 4.61 mmol) was dissolved in TFAA (15.5 g, 73.80 mmol) then fuming nitric acid (3.0 g, 2.0 mL) was added dropwise while cooling with a water bath (with a bit of ice). The water bath was removed and it was stirred for 1 h at room temperature. After that, the reaction mixture was quenched on ice water and the precipitation was filtrated. A mixture of RDX and ADNT was obtained as a colorless solid.

1,3,5-Trinitro-1,3,5–triazinane (RDX)

^{1}H NMR (400 MHz, DMSO-D_6, ppm) δ = 6.13 (s, 6H, −CH_2−).

5-Acetyl-1,3-dinitro-1,3,5-triazinane (ADNT)

^{1}H NMR (400 MHz, DMSO-D_6, ppm) δ = 6.10 (s, 2H, −CH_2−), 5.63 (s, 4H, −CH_2−), 2.17 (s, 3H, −CH_3).

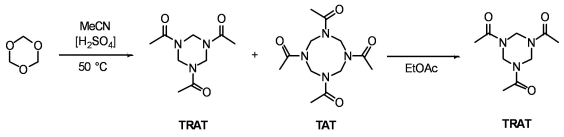
3 | RESULTS AND DISCUSSION

3.1 | Synthesis

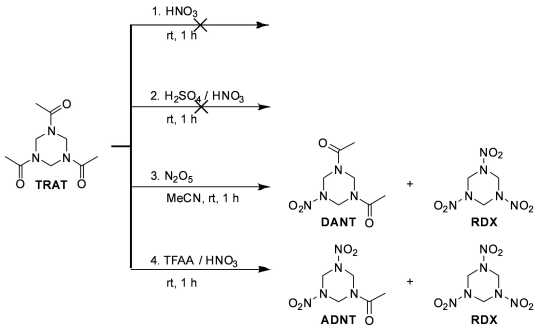
TRAT was synthesized according to a minimally modified method of Meng *et al.* (Scheme 1) [23].

The mechanism of this reaction is also known from the literature [24]. Trioxane first undergoes a tautomeric reaction to form formaldehyde. The presence of acid then protonates formaldehyde to form its oxonium cation, which is in equilibrium with its carbocation. This reacts then with acetonitrile in a condensation reaction and after cyclization, TRAT is formed. However, not only the six-membered ring derivative was obtained, but also traces of the eight-membered ring compound TAT (1,3,5,7-tetraacetycl-1,3,5,7-tetrazocinane) were detected. TRAT could easily be isolated in 50% yield by filtration and washing with a large amount of EtOAc. Purification by simple washing is possible because TAT and TRAT have different solubilities in EtOAc [21].

In the effort to find suitable nitration methods for the nitrolysis of TRAT to RDX, four typical nitration protocols were investigated (Scheme 2). The first implemented protocol was the nitration with nitric acid (100%) from which no product could be obtained, this was also the case for the nitration trial with mixed acid (40% H_2SO_4/



SCHEME 1 Synthesis route towards TRAT and TAT starting from trioxane.



SCHEME 2 Different nitration attempts of TRAT towards RDX.

60% HNO_3). In the third protocol, N_2O_5 in MeCN was used as a nitration agent and a mixture of RDX and the mononitrated 1,3-diacetyl-5-nitro-1,3,5-triazinane (DANT) could be obtained. The received DANT contained about 5% of RDX. So, it can be stated that the nitrolysis by N_2O_5 under the examined conditions was not suited for the synthesis of RDX and DANT can be considered the main product of this reaction. Additionally, the presence of ammonium was observed in the NMR spectrum which was suspected to be a decomposition product stemming from the cleavage of the ring. The fourth implemented protocol with nitration using fuming nitric acid and trifluoroacetic acid anhydride (TFAA) resulted in a mixture of RDX and 5-acetyl-1,3-dinitroo-1,3,5-triazinane (ADNT). In this case 29% RDX content was obtained which is better than in the third nitration trials but also not good enough for industrial application.

In summary, it can be concluded that no optimal, inexpensive and simple way for the nitration of TRAT to RDX could be found. It can be seen that under almost anhydrous conditions, as in protocols 3 and 4, product can be obtained, but in both cases complete conversion into the desired product is not possible. Even tests with longer reaction times or higher reaction temperatures could not improve this result.

3.2 | NMR characterization

The compounds were characterized by ^{1}H NMR spectroscopy. All compounds were measured in deuterated dimethyl sulfoxide (DMSO-D_6).

TRAT and TAT were identified in the crude ^{1}H NMR, see Figure 3. The singlet resonance at 5.21 ppm and 2.11 ppm can be assigned to the methylene ($-CH_2$) and methyl ($-CH_3$) groups TRAT. The remaining two singlet resonances at 4.99 ppm and 2.14 ppm can be assigned to the methylene ($-CH_2$) and methyl ($-CH_3$) groups of TAT. The amount of two signals per compound indicates the symmetrical property resulting in the magnetic equivalence of the -CH_2 and -CH_3 groups in both compounds. The ratio of compound TRAT to TAT can be determined by an equation (1) derived from the formula used to determine purities by q-NMR [25].

$$\%\text{m TRAT} = \frac{\frac{\text{NMR integral}_{\text{TRAT}}}{\text{number of protons}_{\text{TRAT}}} \times \text{M}_{\text{TRAT}}}{\frac{\text{NMR integral}_{\text{TRAT}}}{\text{number of protons}_{\text{TRAT}}} \times \text{M}_{\text{TRAT}} + \frac{\text{NMR integral}_{\text{TAT}}}{\text{number of protons}_{\text{TAT}}} \times \text{M}_{\text{TAT}}} \quad (1)$$

The obtained crude product contained 93% of TRAT and 7% of TAT. Following washing with EtOAc, pure TRAT is visible in the measured ^{1}H NMR spectra.

The NMR spectra after the nitration trial with N_2O_5 shows different signals, see Figure 4. The singlet signal at 6.14 ppm can be assigned to the methylene group of

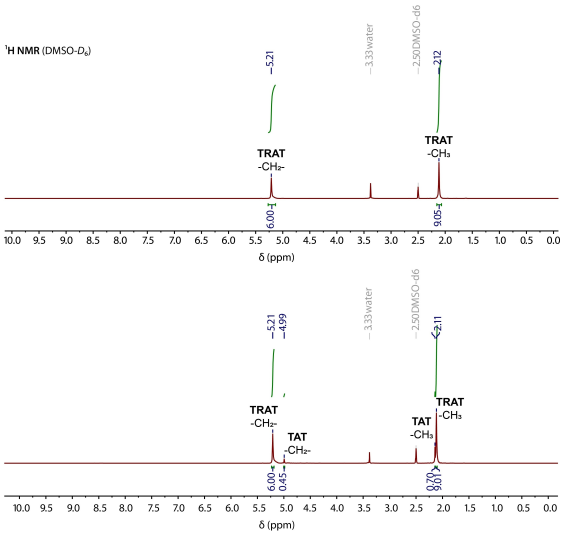


FIGURE 3 NMR spectra of TRAT and TAT.

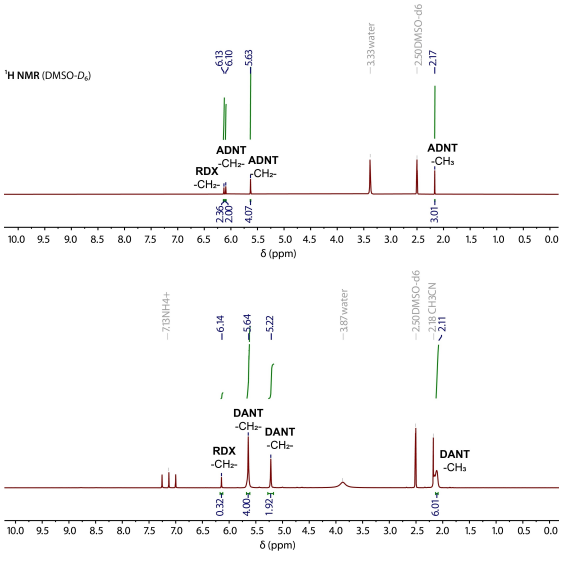


FIGURE 4 NMR spectra after the nitration trials 3 and 4.

RDX. While the singlet signal at 5.64 ppm can be assigned to the protons of the methylene groups in the alpha position to the nitro group of DANT. The singlet signal at 2.11 ppm can be assigned to the methyl groups of the acetyl moiety and the last singlet signal at 5.22 ppm is that of the protons from the methylene group in the alpha position to the carbonyl carbons. A ratio of 5 to 95 can be determined for RDX to DANT by a similar calculation like in equation 1 derived from the formula used to determine purities by *q*-NMR [25]. The triplet signal at 7.13 ppm can be identified as ammonium which indicates decomposition.

After the nitration trial with TFAA and nitric acid, the NMR spectrum shows two compounds. The singlet signal at 6.13 ppm shows again RDX. While the other signals show the presence of ADNT. The singlet at 6.10 ppm can be assigned to the methylene group between the two nitro groups, and the singlet at 5.63 ppm belongs to the remaining two methylene groups from the trioxane ring between the acetyl and the nitro group. The last singlet at 2.17 ppm is from the methyl group of the acetyl moiety. Through the calculation of the ratio using the *q*-NMR formula a ratio of 71% ADNT to 9% RDX can be determined [25].

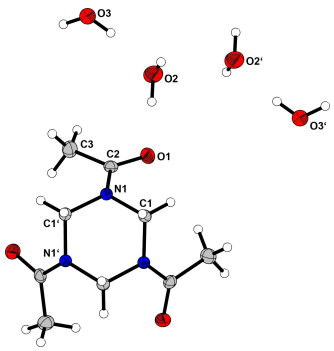


FIGURE 5 Molecular structure of TRAT tetrahydrat.

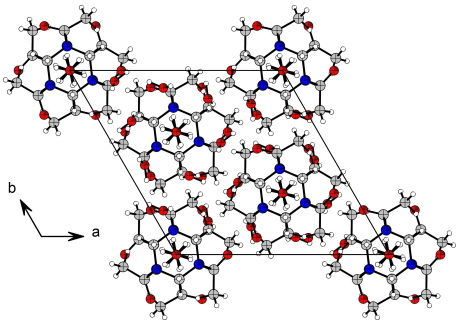


FIGURE 6 Three-dimensional structure of TRAT tetrahydrat along the *c* axis.

3.3 | Crystal structures

For the first time, the single crystal X-ray structure of TRAT tetrahydrate, DANT, and ADNT could be measured at low temperatures. The parameters of the crystal structures are shown in Table 1.

TRAT tetrahydrate crystallizes in the trigonal space group *R*-3, with six molecules in its unit cell and a recalculated density of 1.24 $g\,cm^{-3}$ at room temperature. The crystal structure of TRAT is shown in Figure 5.

Figure 6 shows the three-dimensional structure of TRAT tetrahydrate. It is noticeable that the crystal water is tightly bound between the ring planes as well as between the acetyl groups.

DANT crystallizes in the monoclinic space group $P2_1/c$, with four independent molecules in the asymmetric unit and a recalculated density of 1.40 $g\,cm^{-3}$ at room temperature. The crystal structure of DANT is shown in Figure 7 on the left side while on its right side, the chair configuration of the triazine ring from DANT is highlighted in green. Here it can be seen that the three-ring substituted groups are arranged all in the same direction viewed from the ring plane.

The same arrangement of the substituted groups on the triazine ring can also be seen in the ADNT crystal structure, as shown in Figure 8 highlighted in green on the right. ADNT crystallizes in the monoclinic space group $P2_1/n$, with four molecules in its unit cell and a recalculated density of 1.67 $g\,cm^{-3}$ at room temperature. The crystal structure of ADNT is shown in Figure 8 on the left side.

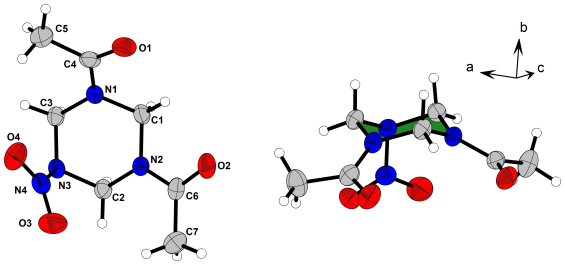


FIGURE 7 Molecular structure of DANT (left) in the crystal structure and chair configuration of its triazinane ring (right).

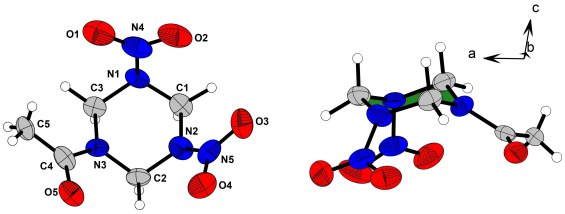


FIGURE 8 Molecular structure of ADNT (left) in the crystal structure and chair configuration of its triazinane ring (right).

TABLE 1 Crystallographic data of TRAT tetrahydrat, DANTand ADNT.

	TRAT · 4 H_2O	DANT	ADNT
Formula	$C_9H_{15}N_3O_3 \cdot 4\ H_2O$	$C_7H_{12}N_4O_4$	$C_5H_9N_5O_5$
FW [g mol^{-1}]	285.30	216.20	219.17
Crystal system	trigonal	monoclinic	monoclinic
Space group	*R*-3	$P2_1/c$	$P2_1$/n
Color/Habit	colorless block	colorless block	colorless plate
Size [mm]	1.00×0.50×0.50	0.08×0.09×0.15	0.50×0.50×0.10
a [Å]	12.0327(13)	7.8404(4)	8.6532(17)
b [Å]	12.0327(13)	8.4558(5)	10.036(3)
c [Å]	17.709(2)	15.1713(8)	9.8564(12)
α [°]	90	90	90
β [°]	90	91.688(2)	99.349(15)
γ [°]	120	90	90
V [Å^3]	2220.5(6)	1005.37(9)	844.6(3)
Z	6	4	4
ρ_{calc} [g cm^{-3}]	1.280	1.428	1.724
μ [mm^{-1}]	0.109	0.118	0.153
F (000)	924	456	456
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	96	173	92
θ Min-Max [°]	3.0, 26.4	2.8, 27.5	2.9, 26.4
Dataset	−9:14; −14:6; −22:11	−10:9; −10:10; −19:19	−10:10; −12:8; −10:12
Reflections coll.	1461	16834	3765
Independent refl.	999	2296	1734
R_{int}	0.011	0.047	0.060
Parameters	90	184	148
*R*1 (obs)[a]	0.0359	0.0390	0.0679
wR2 (all data)[b]	0.0978	0.1017	0.1555
Resd. Dens. [e Å^{-3}]	−0.17, 0.31	−0.19, 0.20	−0.24, 0.33
Device type	Xcalibur, Sapphire 3	D8 Venture	Xcalibur, Sapphire 3
Solution	SHELXT 2018/2	SHELXT 2018/2	SHELXT 2018/2
Refinement	ShelXL 2018/3	ShelXL 2018/3	ShelXL 2018/3
CCDC	2241832	2241833	2241834
Absorption corr.	multi-scan	multi-scan	multi-scan

[a] $R1 = \Sigma||F0|-|Fc||/\Sigma|F0|$

[b] $wR2 = [\Sigma[w(F02-Fc2)2]/\Sigma[w(F0)2]]1/2$; $w = [\sigma c2(F02)+(xP)2+yP]-1$ and $P = (F02+2Fc2)/3$.

3.4 | Energetic properties

The energetic properties were calculated using the EXPLO5 code version 6.06.01 [26] and can be found in Table 2. The EXPLO5 calculations are based on the X-ray density recalculated to room temperature, as well as the enthalpy of formation calculated on CBS-4 M level using the Gaussian software. [27]

Comparing the energetic parameters of the three compounds, it can be seen that, as expected, the calculated detonation velocity decreases from RDX via ADNT to DANT. ADNT with a velocity of detonation of 7518 m s^{-1} still has a moderate performance which is better than that of TNT (6793 m s^{-1}) at a comparable density [12]. In contrast, the value for the mono-nitro derivative DANT with 5879 m s^{-1} is clearly too low for use as an energetic material.

4 | CONCLUSIONS

The objective of this work was to assess the synthesis of RDX *via* the intermediate TRAT (1,3,5-triacetyl-1,3,5-triazinane) as a potential alternative industrial production

TABLE 2 Energetic properties of compounds DANT, ADNT and RDX.

	DANT	ADNT	RDX [12]
Formula	$C_7H_{12}N_4O_4$	$C_5H_9N_5O_5$	$C_3H_6N_6O_6$
FW [g mol^{-1}]	216.19	219.16	222.12
$\rho_{calc.}$ (298 K) [g cm^{-3}] [a]	1.40	1.67	1.80
$T_{melt.}$ [°C][b]	85	143	188
$T_{dec.}$ [°C][c]	177	228	209
$\Delta_f H°$ [kJ mol^{-1}][d]	−412.9	−165.8	70.3
EXPLO5 V6.06.01			
P_{CJ} [GPa][e]	11.7	20.9	33.6
V_{det} [m s^{-1}][f]	5879	7518	8794
$-\Delta_{ex}U°$ [kJ kg^{-1}][g]	2158	3982	5717
T_{det} [K][h]	1741	2689	3734
V_0 [m^3 kg^{-1}][i]	775	798	784

[a] X-ray density converted to RT
[b] melting point indicated by endothermic event according to DTA (onset temperatures at a heating rate of 5 °C min^{-1})
[c] temperature of decomposition indicated by exothermic event according to DTA (onset temperatures at a heating rate of 5 °C min^{-1})
[d] calculated (CBS-4 M) heat of formation converted to the solid state HOF
[e] detonation pressure
[f] detonation velocity
[g] Energy of explosion
[h] Explosion temperature
[i] Assuming only gaseous products.

method. This route was stated to be a promising method for the production of pure RDX (without HMX impurities) under industrial conditions [21]. Therefore, this work was made in an effort, to evaluate the synthesis route with regard to its efficiency, to identify suitable nitration methods, and to estimate its potential.

This method has various advantages, including cheap starting materials and reactants as well as easy separation of TAT (1,3,5,7-Tetraacetyl-1,3,5,7-tetrazocinane) and TRAT by solubility differences. Due to the similar chemical and physical properties of RDX and HMX the isolation of both is very hard, so it would be favorable to separate the precursor TAT and TRAT from each other to obtain pure RDX in the next step. This aspect was successfully confirmed in this work where no trace of TAT was detected in TRAT following washing with ethyl acetate. However, for the synthesis of TRAT in this work only a moderate yield of 50% was obtained. This presents a serious obstacle and suggests the need for further optimization or a change in the reaction and the reactants.

The main challenge of this work was the search for a feasible nitration method from TRAT to RDX, in the evaluation process this was identified as the main challenge of this method. Every tested method of nitration either gives no nitration product or merely leads to incomplete nitration with a low percentage of RDX. Further optimization of the reaction conditions and other methods could increase the ratio of RDX but for this process to be viable solely RDX has to be obtained. Otherwise, the main objective to yield pure RDX is missed. The option to develop a purification method to isolate RDX from the incompletely nitrated by-products would run the risk of making the process too complicated and therefore inferior to the well-established methods of the Bachmann and Woolwich processes.

However, from an academic standpoint, this work resulted not only in the determination of the undefined crystal structure of TRAT tetrahydrate, but also in the first-ever recorded synthesis of DANT and the determination of its crystal structure as well as the low-temperature measured crystal structure of ADNT. This may advance the understanding of this process and promote its improvement to make it a feasible alternative.

In conclusion, the production of RDX *via* TRAT holds great potential but is not yet a viable method for industrial application.

ACKNOWLEDGMENTS

For financial support of this work the Ludwig Maximilian University (LMU), EMTO GmbH, and BIAZZI SA are gratefully acknowledged.

DATA AVAILABILITY STATEMENT

Data may be requested via the authors.

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How to cite this article: Klapötke T. M., Lechner J. T., Stanislawski L. W. B., Stierstorfer J., Mühlemann M. & Lemarchand G. (2023). Investigation of a new promising process for the RDX synthesis *via* 1,3,5-triacetyl-1,3,5-triazinane (TRAT). *Propellants, Explosives, Pyrotechnics*, *48*, e202300062. https://doi.org/10.1002/prep.202300062