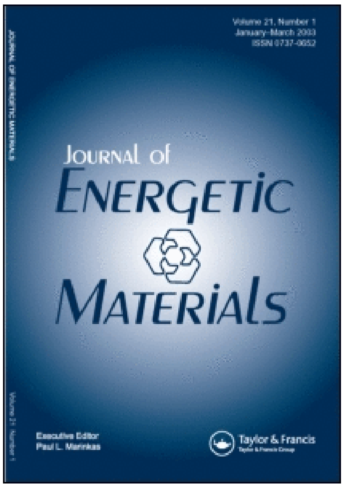

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1,3,3-trinitroazetidine (TNAZ). Part I. Syntheses and properties

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Part I. Syntheses and Properties.

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ABSTRACT

Review of more than sixteen routes for **TNAZ** synthesis is presented. The total yields of the most technologically attractive of thees does not exceed 30 % of theory. It is stated that **TNAZ** is highly energetic material more powerful than RDX, which may be less vulnerable than most other nitramines, and which is suitable for applications as a castable explosive as well as a plasticizer. However, a relatively high vapour pressure, volume contraction and formation of shrinkage cavities in the solidification of its melt can be a minor disadvantage of **TNAZ**.

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INTRODUCTION

Nitramines continue to be a source of new explosives characterised by high energy content[1-5]. One of the substances of this type that has been given attention in systematic and practical ways since 1990 is 1,3,3-trinitroazetidine (**TNAZ**)[1-6]. Therefore, the following text presents a survey of syntheses and some important properties of this technologically interesting nitramine.

SYNTHESES OF TNAZ

1,3,3-Trinitroazetidine (**TNAZ**) was first prepared in 1983 at Fluorochem, Inc[1]. The open literature describes a number of its syntheses at the present. The survey is presented in Schemes 1 and 2. The individual procedures differ in using different starting materials, in the way of constructing the azetidine cycle, and the way of introducing nitro groups into the molecule.

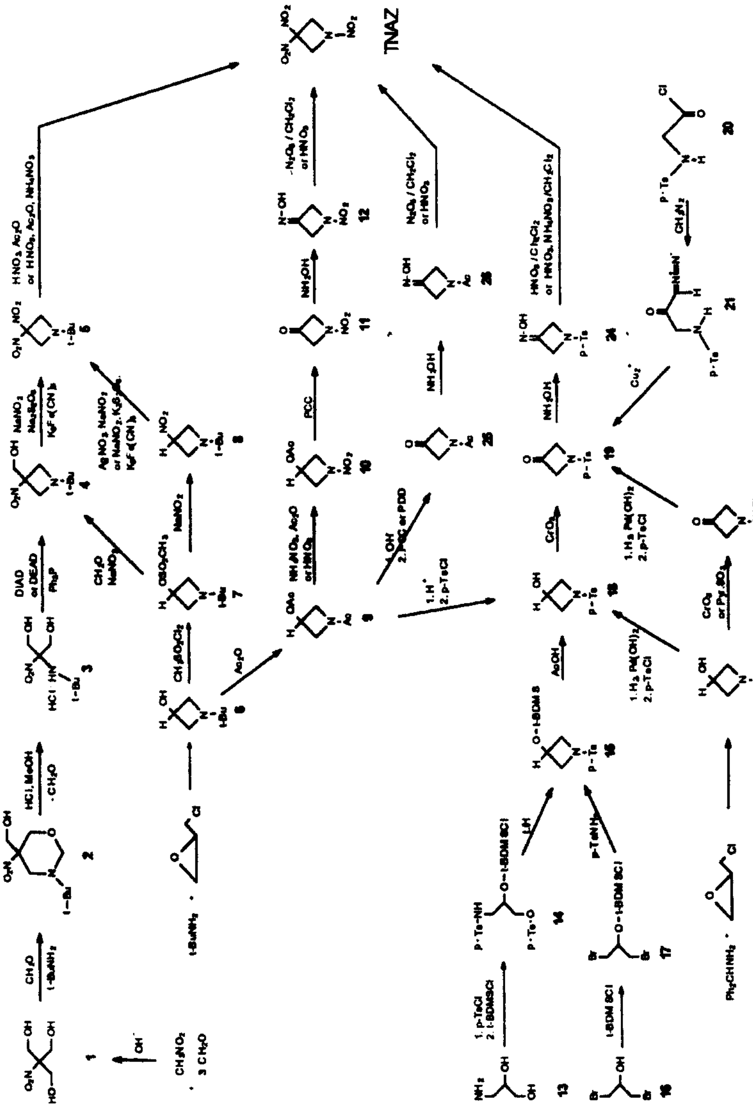
The base catalysed reaction of nitromethane with three molecules of formaldehyde produces *tris*(hydroxymethyl)nitromethane (**1**)[7,8], which reacts with another molecule of formaldehyde and with *tert*-butylamine to give 3-*tert*-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine (**2**)[9,10]. Compound **2** is then heated in methanol with concentrated hydrogenchloride and provides a linear product, 2-*tert*-butylaminomethyl-2-nitro-1,3-propanediol hydrochloride (**3**)[10-12], which is subsequently cyclised by applying diethyl azodicarboxylate (DEAD) and triphenylphosphine[12] or diisopropyl azodicarboxylate (DIAD) and triphenylphosphine[10,11], and produces 1-*tert*-butyl-3-hydroxymethyl-3-nitroazetidine (**4**). This procedure introduces the first nitro group into the azetidine molecule as early as the ring closure stage. The second nitro group is introduced by oxidative nitrolysis of compound **4** using a mixture of sodium nitrite, potassium ferricyanide and sodium persulfate[10-12]. The product is 1-*tert*-butyl-3,3-dinitroazetidine (**5**). Substance **5** is nitrolysed to **TNAZ** by a mixture of nitric acid and acetic anhydride[13,14], or a mixture of nitric acid, acetic anhydride, and ammonium nitrate[10,14].

Another approach to azetidine cycle consists of a condensation reaction of epichlorhydrin with *tert*-butylamine [15-17]. The reaction produces 1-*tert*-butyl-azetidin-3-ol (**6**), which in a subsequent step undergoes a reaction with methanesulfonyl chloride to give 1-*tert*-butyl-3-methanesulfonyloxyazetidine (**7**)[15]. Substance **7** can be transformed into **4**[18] by reaction with formaldehyde and sodium nitrite, or it can provide 1-*tert*-butyl-3-nitroazetidine (**8**)[13] by reaction with sodium nitrite. Compound **8** is then transformed into **5**[13] by oxidative nitration[19,20] with silver nitrate and natrium nitrite, or with a mixture of sodium nitrite, potassium ferricyanide, and sodium persulfate.

1-*tert*-Butylazetidin-3-ol (**6**) reacts with acetic anhydride to give 1-acetyl-3-acetoxyazetidine (**9**)[14], which is then nitrolysed with a mixture of ammonium nitrate and acetic anhydride, or with fuming nitric acid to give 1-nitro-3-acetoxyazetidine (**10**)[21,22]. Compound **10** is subsequently hydrolysed and oxidised with pyridinium chlorochromate (PCC) to give 1-nitro-azetidin-3-one (**11**), which reacts with hydroxylamine to give 1-nitro-azetidin-3-one oxime (**12**). Compound **12** is submitted to oxidative nitration to **TNAZ** with a dinitrogen pentoxide in methylenedichloride or with fuming nitric acid[21,22].

Another starting material for synthesis of **TNAZ** is 3-aminopropane-1,2-diol (**13**). Its reaction with *p*-toluenesulfonyl chloride and *tert*-butyldimethylsilyl chloride (*t*-BDMSCl) produces 3-*p*-toluenesulfonamido-2-*tert*-butyldimethyl-silyloxy-1-(*p*-toluenesulfonyl)-oxypro-pane (**14**), which on cyclization induced by lithium hydride provides 1-(*p*-toluenesulfonyl)-3-*tert*-butyldimethylsilyloxy-azetidine (**15**)[23,24]. Compound **15** can alternatively be prepared from 1,3-dibromopropan-2-ol (**16**), which in reaction with *tert*-butyldimethylsilyl chloride provides 1,3-dibromo-2-*tert*-butyldimethylsilyloxy-propane (**17**). The reaction of compound **17** with *p*-toluenesulfonamide induces its ring closure to 1-(*p*-toluenesulfonyl)-3-*tert*-butyldimethylsilyloxyazetidine (**15**)[23,24]. Hydrolysis of compound **15** with acetic acid gives 1-(*p*-toluenesulfonyl)-azetidin-3-ol (**18**). Compound **18** can also be prepared from compound **9** by hydrolysis and a subsequent reaction with *p*-toluenesulfonyl chloride. Compound **18** is further oxidised with chromium(VI) oxide to give 1-(*p*-toluenesulfonyl)-azetidin-3-one (**19**)[23,24]. Compound **19** can be prepared alternatively by a reaction of *N*-(*p*-toluenesulfonyl)-2-aminoacetyl chloride (**20**) with diazomethane and the subsequent ring closure of diazoketone **21**[23,24]. In the syntheses of compounds **18** and **19**, it is also possible to adopt epichlorhydrin and benzhydrylamine as the starting materials. Their condensation leads to 1-benzhydryl-azetidin-3-ol (**22**)[25]. Hydrogenolysis of compound **22** and the subsequent reaction of the intermediate with *p*-toluenesulfonyl chloride gives compound **18**. Beside that, compound **22** can be oxidised with chromium(VI) oxide[26,27] or pyridine sulphur trioxide complex[26,28] to give 1-benzhydryl-azetidin-3-one (**23**). Hydrogenolysis of compound **23** and the subsequent reaction with *p*-toluenesulfonyl chloride produces compound **19**, which in reaction with hydroxylamine gives 1-(*p*-toluenesulfonyl)-azetidin-3-one oxime (**24**)[23,24,26]. The latter compound (**24**) can be oxidatively nitrated and simultaneously nitrolysed with a mixture of nitric acid and dichloromethane[23], or with a mixture of nitric acid, ammonium nitrate, and dichloromethane[24], to give **TNAZ**. The synthesis thus performed has the advantage in simultaneously (in one step) introducing all three nitro groups of **TNAZ** into the molecule of substituted azetidine. In a similar way, it is possible to prepare **TNAZ** if one starts with 1-acetyl-3-acetoxyazetidine (**9**), which on alkaline hydrolysis and subsequent oxidation with pyridinium chlorochromate (PCC)[21] or pyridinium dichromate (PDD)[22] provides 1-acetyl-azetidin-3-one (**25**), which reacts with hydroxylamine to give 1-acetyl-azetidin-3-one oxime (**26**). The latter compound (**26**) is simultaneously oxidatively nitrated and nitrolysed with dinitrogen pentoxide in dichloromethane or with nitric acid to give **TNAZ**[21].

Another approach to synthesis of **TNAZ** is represented in Scheme 2. The reactions proceede *via* the bicyclic compounds 1-azabicyclo[1.1.0]butane (**27**) and 1-aza-3-(bromomethyl)bicyclo[1.1.0]butane (**37**). Compound **27** can be prepared as follows: (a) by reaction of *N*-chlorosuccinimide (**28**) with allylamine[29], (b) by bromination of 2-amino-1,3-propanediol (**29**) and bicyclisation of the intermediate 1,3-dibromopropyl-2-amine hydrobromide (**30**)[29,30], (c) by chlorination of 1-*tert*-butyl-azetidin-3-ol (**6**) to 1-*tert*-butyl-3-chloroazetidine (**31**), subsequent acetylation of compound **31** to 1-acetyl-3-chloroazetidine (**32**) and final bicyclisation of the latter compound (**32**) with potassium hydroxide[14], or (d) by hydrolysis and subsequent bicyclisation of 1-acetyl-3-acetoxyazetidine (**9**)[14]. 1-Azabicyclo[1.1.0]butane (**27**) then reacts with sodium nitrite to give 1-nitroso-3-nitroazetidine (**33**) whose nitrolysis with a mixture of nitric acid and trifluoroacetic anhydride leads to 1,3-dinitroazetidine (**34**); its oxidative nitration provides **TNAZ**[29,30]. The starting material for 1-aza-3-(bromomethyl)bicyclo[1.1.0]butane (**37**) is *tris*(methylol)aminomethane (**35**) whose bromination in acid medium gives *tris*(bromomethyl)aminomethane hydrobromide (**36**). The bicyclisation of compound **36** produces 1-aza-3-(bromomethyl)bicyclo[1.1.0]butane (**37**). Compound **37** (in analogy to **27**) is transformed to **TNAZ**[30] by reaction with sodium nitrite giving 1-nitroso-3-bromomethyl-3-nitroazetidine (**38**) whose nitrolysis gives 3-bromomethyl-1,3-dinitroazetidine (**39**), which is hydrolysed to 3-hydroxymethyl-1,3-dinitroazetidine (**40**). Oxidative nitrolysis of compound **40** provides TNAZ.


TNAZ
OH⁻
CH3NO2 + 3 CH2O
CH2O, t-BuNH2
HCl, MeOH, -CH2O
DIAD or DEAD, Ph3P
NaNO2, Na2S2O8, K3Fe(CN)6
HNO3, Ac2O or HNO3, Ac2O, NH4NO3
CH2O, NaNO2
AgNO3, NaNO2 or NaNO2, K2S2O8, K3Fe(CN)6
t-BuNH2 +
CH3SO2Cl
NaNO2
Ac2O
NH4NO3, Ac2O or HNO3
PCC
NH2OH
N2O5 / CH2Cl2 or HNO3
1. OH⁻ 2. PCC or PDC
1. H⁺ 2. p-TsCl
N2O5 / CH2Cl2 or HNO3
1. p-TsCl 2. t-BDMSCl
t-BDMSCl
LiH
p-TsNH2
AcOH
CrO3
HNO3 / CH2Cl2 or HNO3, NH4NO3/CH2Cl2
Cu2+
CH2N2
1. H2 Pd(OH)2 2. p-TsCl
CrO3 or Py.SO3
Ph2CHNH2 +
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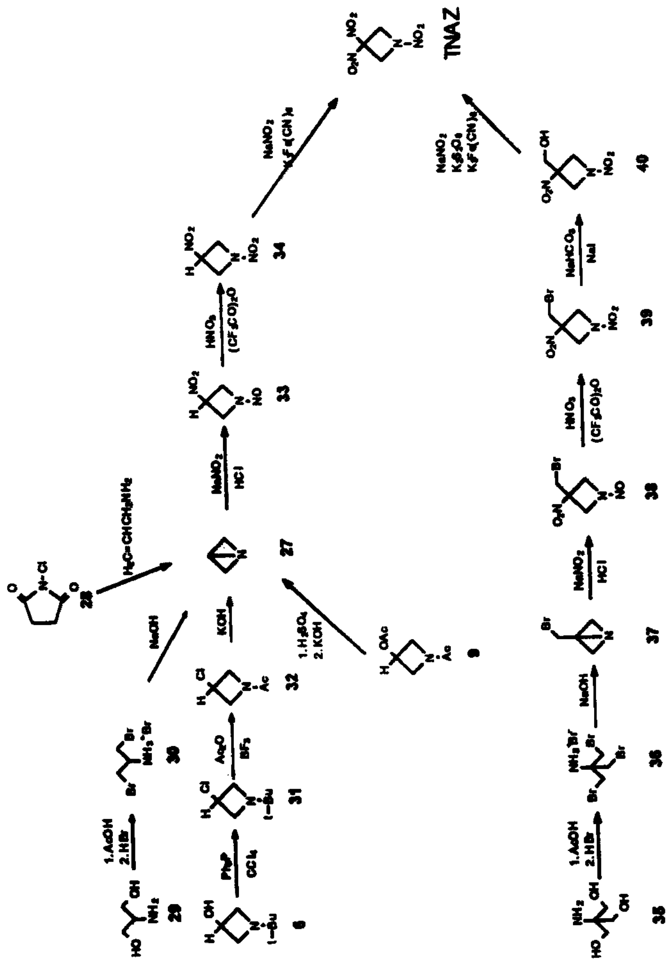
SCHEME 1



SCHEME 2

Notes to schemes 1 and 2:

Ac -acetyl
t-Bu - tert-butyl
t-BDMSCl - tert-butyldimethylsilylchloride
DEAD - diethylazodicarboxylate
DIAD - diisopropylazodicarboxylate
Me - methyl

PCC - pyridinium chlorochromate
PDD - pyridinium dichromate
Ph - phenyl
p-Ts - p-toluensulfonylchloride

The procedure starting from nitromethane and formaldehyde[10,12], in which the problems of recycling of raw materials and of waste water[11] have been solved, and partially also the procedure starting from epichlorhydrin and *tert*-butylamin *via* compound **4**[18] are applicable on technological scale. The overall yields in most cases, however, do not exceed 30 % of theory[6,10] even if 57 % theory is indicated in the one case[11]. Other procedures are only applicable to laboratory syntheses because of their lower yields and the processes involved are inapplicable on laboratory scale.

The price of the laboratory prepared products is currently about of $ 5,- per gram[6] at the present. This is so far the greatest drawback to large scale implementation of **TNAZ** in military systems. However, the activities continue in the search for an alternative production of TNAZ that would substantially reduce manufacturing cost.

PROPERTIES OF TNAZ

Physico-chemical properties

1,312,3-Trinitroazetidine is white crystalline solid, soluble in acetone, methanol, ethanol, tetrachloromethane, and cyclohexanone[13,31,32]. A survey of its physico-chemical characteristics is presented in Table 1. **TNAZ** has a relatively high vapour pressure[44]. The solidification of its melt is accompanied by high volume contraction[41] and formation of shrinkage cavities (10 – 12% porosity)[44]. These excessive vapour pressure and charge porosity can be reduced by addition an effective amount of N-methyl-4-nitroaniline to a melt **TNAZ**[44].

The bond length and bond angle values of **TNAZ** were specified by means of X-ray analysis[6,13]: N–N bond length in nitramino group is 0.1351 nm, the C–NO_2 bond lengths at position 3 are not equivalent (0.1517 nm and 0.1493 nm); the bond angles C–C–C (90.3°), C–N(aza)–C (95.1°), and N(aza)–C–C (86.5° and 86.6°) of azetidine ring are considerably deformed[3,13]. The substance exists in two crystal modifications[31,37]: **TNAZ** I stable and with higher density, and **TNAZ** II unstable and with lower density. The crystals of required size can be obtained by crystallisation from saturated **TNAZ** solutions using an ultra-centrifuge[52,53] which simultaneously minimises formation of defects in the crystals.

TABLE 1: Survey of the basic physico-chemical properties of **TNAZ**

Property	Value	Ref.
Density (kg.m^{-3})	1830 – 1840 1554 at 105 °C 1522 at 120 °C	3,5 41 41
Melting point (°C)	97.27, 98.68, 99.3, 99.45, 99.7, 101 melting range 99.0-99.7	33,35,36,4,2,37,39 6,38 39
Boiling point (°C)	252	40
Heat of melting (kJ.mol^{-1})	30.31 28.35	39 6
Heat of sublimation (kJ.mol^{-1})	63.22	38,40,42
Heat of formation (kJ.mol^{-1})	8.79, 11.76, 26.81, 27.66, 36.4	4,4,36,37,43

TNAZ forms eutectic mixtures with some energetic materials; a survey is given in Table 2. Admixtures of **TNAZ** with TNT enables to attain any aimed performances by "single explosive"[6]. The literature also presents information about the molecular complexes of **TNAZ** with β-cyclodextrin[43-47] and with ammonium and sodium salts of dinitraminic acid[48].

TABLE 2: Eutectic mixtures of **TNAZ**

Additive	Melting point of additive (°C)	Melting point of eutectic (°C)	**TNAZ** content in eutectic (mol. %)	Ref.
TNT	80.6	60.6	35.3	31,35,37
Tetryl	129.5	81.5-81.6	63.3-65.0	33,35
HMX	284.1	95.9	97.87	33
2,4-Dinitroimidazole	277.9	~96.2	97.67	33
N-Acetyl-3,3-dinitro-azetidine	111.0-114.4	74.2-78.6	61.7-66.0	37
1„3-Dinitro-3-(1,3-dinitroazetidin-3-yl)-azetidine	171-173	90	87.5	36

Spectra

The published IR spectra of **TNAZ** obtained by the KBr disc technique[6,49] show distinct signals in the fingerprint area, the C–H and N–O/NO_2 vibrations being clearly identifiable. The occurrence of weak C–H signals in the IR spectrum above 3000 cm^{-1} is connected with the heterocyclic ring strain in **TNAZ**[6].

The singlet in the ^{1}H NMR spectrum at 5.30 ppm (according to Ref. 6) and at 5.39 ppm (according to Ref. 50) was specified for the chemically and magnetically equivalent protons in **TNAZ** molecule. The carbon atoms at the 2 and 4 positions of azetidine cycle show a ^{13}C NMR chemical shift of 63.5 ppm (according to Ref. 6) or 64.0 ppm (according to Ref. 50), and the carbon atom at 3 position shows a shift of 104 ppm[6] or 104.2 ppm[50]. The ^{15}N NMR spectrum of **TNAZ**[50] exhibits the chemical shifts of nitrogen atoms of 3-nitro groups at –16.7 ppm and those of nitramino group at –20.5 ppm; the aza nitrogen atom of azetidine cycle exhibits the shift value of –228.7 ppm[50].

Mass spectral fragmentation of **TNAZ**[51] shows that its major pathways involve the loss of NO_2 or nitrous acid from the dinitromethylene group followed by a loss of nitro group or NO from the nitramine grouping. The peak at m/z 46, $[NO_2]^+$ (the base peak), resulted primarily from N-N bond scission and the peak at m/z 30, $[NO]^+$, was equally likely to come from any nitro group.

The X-ray diffraction of **TNAZ** within the temperature interval from –70 to 100 °C forms a part of paper[6]. The parameters of crystal lattice determined on its basis are identical with the data published earlier[13].

Thermal Reactivity

The literature states that **TNAZ** is thermally more stable than RDX (i. e. 1,3,5-trinitro-1,3,5-perhydrotriazine), but more reactive than HMX[4,6,29] (i. e.

1,3,5,7-tetranitro-1,3,5,7-perhydrotetrazocine). Several papers deal with studies of kinetics and mechanism of thermal decomposition of **TNAZ** in gas phase[38,54,55], liquid phase[6,39,56,57], in 0.01 – 1.0 % solutions in benzene, water, acetone, methanol[56,57], and by means of SCF-MO-AMI calculations[58]. An attention was also paid to laser-induced pyrolysis of TNAZ[60] and to main intermediate of **TNAZ** thermal decomposition[57,59]. Results of vacuum stability test of pure **TNAZ** and some its mixtures with HNIW and HMX are a part of paper[41]. As the reactivity is very important for practical exploitation of **TNAZ**, it will be evaluated in the second part of this paper[61].

Sensitivity to Stimuli

The sensitivity to thermal, mechanical and electric stimuli can be documented by the critical temperature T_c, by the shock sensitivity (as the fall height $h_{50\%}$ and energy E_{dr} determined in the sense of Ref. 62) and electric spark sensitivity (the spark energy E_{ES} determined in the sense of Ref. 63). A survey of the respective values for TNAZ in comparison with those of some important explosives is presented in Table 3.

In the slow and fast cook-off tests, the detonations of **TNAZ** were recorded in the temperature range of 198 – 214 °C[73]. The sensitivity of **TNAZ** to friction (8.9 – 11.6 kg)[4] is comparable with the sensitivity of HMX (11.6 kg)[4]. Pure **TNAZ** is more shock-sensitive than the explosives based on HMX but less sensitive than analogous PETN (i. e. pentaerythritol tetranitrate) mixtures[74]. An addition of 5 – 25 % wt. nitroaromatic amine (preferably *N*-methyl-*p*-nitroaniline) to **TNAZ** can reduce the shock sensitivity of its cast mixtures[44], due to the favourable influence of the additive on **TNAZ** nucleation in its melt solidification. The ionisation potential of **TNAZ** (10.36 eV) and that of its *N*-nitroso analogue NDNAZ (9.52 eV) are known too[75].

TABLE 3: Survey of the critical temperatures T_c, sensitivities to impact ($h_{50\%}$ and E_{dr}) and electric spark (E_{ES}) of **TNAZ** and technologically attractive explosives.

Explosive	Critical temperature		Impact sensitivity			Electric spark sensitivity	
	T_c (°C)	Ref.	$h_{50\%}$ (cm)	E_{dr} (J)	Ref.	E_{ES} (J)	Ref.
Composition C-4	210	63		24.0	a	>64.80	63
TNT	214	65,66	160	39.2	67	4.10	68,69,71
TETRYL	184	64	32	7.8	67	5.49	68,70,71
PETN	197	65,68	12	2.9	67	1.74	71
RDX	214	65.66	24	5.9	67	2.49	68,70,71
HMX	258	65,66	26	6.4	67	2.92	68,70,71
α–HNIW	203	64	20.7^{b}	10.2^{b}	72	6.23	64
ε–HNIW	221	64	24.2^{b}	11.9^{b}	72	4.70	64
TNAZ	238^{c}	40	28-29	6.9-7.1	4	8.76	50
	235	d					

Notes:

a) the value given by the producer, i. e. CHEMKO, SK-072 22 Strážske, Slovakia,
b) determined with a 5 kg hammer
c) determined by means of DSC
d) calculated from the first maximum T_m of exotermic DTA curve by means of a calibration curve of "T_c-T_m" from Ref. 64

Composition C-4: a plastic explosive containing of 91 % wt. RDX
TNT: 2,4,6-trinitrotoluene
TETRYL: 1-methylnitramino-2,4,6-trinitrobenzene
PETN: penterythritol tetranitrate
RDX: 1,3,5-trinitro-1,3,5-perhydrotriazine
HMX: 1,3,5,7-tetranitro-1,3,5,7-perhydrotetrazocine
HNIW: 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane

Explosive Properties

The results of detonation calorimetry indicate that TNAZ possesses 96% of HMX energy and 150% of TNT energy[4]. It is suitable for application as castable explosive[6]. As an ingredient in solid rocket and gun propellants can be comparable with that of HNIW[6]. A survey of explosive characteristics of TNAZ compared with those of some other important explosives is given in Table 4. Here the values of detonation velocity, $D_{calcd.}$, maximum heat of detonation, Q_{max}, detonation pressure, P_{CJ}, and volume of gaseous products were calculated by EXPLO5 computer code[79] using the following constants in BKW equation of state[80]: $\alpha = 0.5$, $\beta = 0.176$, $\kappa = 14.71$ and $\theta = 6620$. As the Table 4 shows, the TNAZ detonation products are relatively hot, making it attractive as an ingredient in composite explosives[4].

Analytical

An excellent method of qualitative and quantitative analysis of TNAZ and/or the compositions that contain TNAZ is HPLC[76,77] with the detection limit below 5 ng[77]. Micellar electrokinetic capillary chromatography (MECC) has also been used for these purposes[78]. The above-mentioned spectral methods[6,49,51] have been used mainly for analyses of the molecular structure of TNAZ.

CONCLUSION

More than sixteen routes are published for synthesis of 1,3,3-trinitroazetidine (TNAZ) in the open literature. However, only the procedure starting from nitromethane and formaldehyde[6,10,11], and partially also the procedure starting from epichlorhydrin and *tert*-butylamin *via* 1-*tert*-butyl-3-hydroxymethyl-3-nitroazetidine[18], are applicable on technological scale. Overall yields of the common syntheses of TNAZ in most cases do not exceed 30 % of theory at the present, even if 57 % of theory was indicated in the one case[11]. Therefore, the total costs of these syntheses are still high[1,6].

Relatively small molecule of TNAZ, deformation of its skeleton[3,13] together with its energy content, bring some advantages, but also some problems. It is, above all, a highly energetic material, slightly more powerful than RDX, possessing 150 % energy of TNT[4]. Unlike most nitramines, it may be less vulnerable and is able for application as a castable explosive as well as a plasticizer. A relatively high vapour pressure[44], volume contraction[41] and formation of shrinkage cavities[44] in the solidification of its melt can be the minor disadvantages of TNAZ. These undesirable manifestations can be, however, reduced by addition of an effective amount of nitro-substituted aromatic amine to a melt **TNAZ**[44].

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