

TEX – 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane – Review of a Promising High Density Insensitive Energetic Material

Ernst-Christian Koch^{*,[a]}Dedicated to Dr. Bernard E. Douda on the Occasion of his 85th Birthday

Abstract: The title compound 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane – often referred to as TEX – is a very promising newcomer in the field of insensitive explosives. It is easily synthesized with good yield from cheap starting materials. TEX offers a respectable high ambient temperature crystal density (1.985 g cm⁻³) and

hence good detonation velocity and pressure but is fairly insensitive towards mechanical and thermal stimuli. It has a large critical diameter and is advantageously used in large charges. 76 references to the public domain are given.

Keywords: Explosives • 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane • Insensitive munitions • TEX • Synthesis

1 Introduction

The safety and sensitivity of ammunition are closely related to the properties of the energetic material used therein. Hence inherently insensitive explosives allow for a greater degree of freedom in design of insensitive munitions (IM) whereas highly sensitive energetic materials require all kinds of complementary measures to render munitions compliant with the IM requirements [1] thus making munitions more costly. In research for insensitive energetic materials the community is considering a number of strategies. These comprise the use of binders and surfactants with existing sensitive high explosives such as RDX and HMX to achieve an improved IM signature [2,3]. They include the particle engineering of the existing high explosives in order to reduce their sensitivity [4,5] and the use of nanometric particles, which inherently show a reduced sensitivity to mechanical stimuli [6,7]. Whereas the use of binders and particle engineering are feasible measures with respect to large scale use of HE in general purpose bombs and other large warheads the use of nanomaterials is cost-prohibitive for those applications and will probably be also for small scale use in boosters and transfer trains. Hence new materials have to be considered, which complement the range of sensitive high explosives.

Apart from having a significantly higher activation barrier to decomposition than conventional high explosives, insensitive high explosives nonetheless should possess sufficient energy content to be a close match with standard HE. Whereas it is definitely no issue in finding less sensitive materials by simply tailoring the type and reducing the number of explosophoric groups in a certain molecule, retaining the energy content of an insensitive explosive is

definitely an issue. It is hence that in the quest for new insensitive high explosives achieving high density plays a paramount role. This is because the detonation velocity, V_d (m s⁻¹), of an energetic material correlates linearly with the density, whereas the detonation pressure, P_d (GPa), correlates with its square.

Currently 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane (Figure 1 a) – better known as CL-20 – is the most dense stable CHNO compound with an ambient density of the ϵ -polymorph of $\rho = 2.044$ g cm⁻³ [8]. The high density of CL-20 is mainly due to the isowurtzite cage structure of the compound. However CL-20 is very sensitive to both friction (64 N) and impact (4 J) and to thermal stress [8] which is believed to result from steric

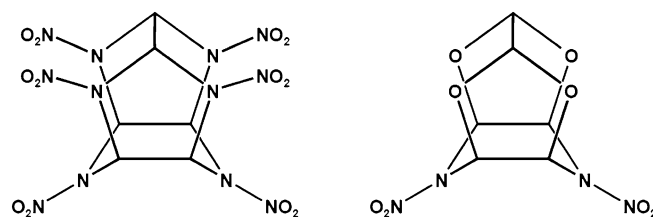


Figure 1. Molecular structures of (left) CL-20 and (right) TEX (1).

[a] E.-C. Koch
Cranfield University & Defence Academy of the United Kingdom
Centre for Defence Chemistry
Swindon, Shrivenham SN68LA, UK
*e-mail: e-c.koch@cranfield.ac.uk

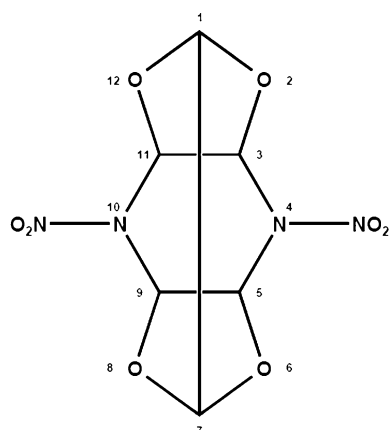


Figure 2. Projection of TEX.

strain of the nitramine groups. Both the exceptional sensitivity as well as the high production cost currently impede large scale use of CL-20 and restrict its use to small items.

A prominent “relative” to CL-20 is 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane (1), commonly abbreviated TEX. TEX derives from CL-20 by replacement of four nitramine groups by ether bridges [9] (Figure 1b). As TEX possesses the same isowurzitane cage structure as CL-20 it conserves the very high ambient temperature density of $\rho = 1.985 \text{ g cm}^{-3}$, however due to absence of sterically demanding nitramine groups reduces its sensitivity greatly and makes this an interesting insensitive energetic material.

Yu and co-workers assert to have synthesized TEX then designated **797** already in 1979 [10]. Lubanova et al. also assert to have patented the synthesis of TEX as early as 1985 [11]. The first unambiguous reference to TEX however has been made by Boyer and co-workers in 1990 in an openly accessible journal [12].

Although three reviews on TEX are available from the public domain [13–15] they are partly outdated and do not represent the state of knowledge. Hence this review aims at summarizing up-to date facts on the synthesis, structure, sensitivity, performance and toxicity of TEX.

The systematic nomenclature of TEX (1), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane, is explained with a projection of the main ring in Figure 2.

2 Physical and Chemical Properties

4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]-dodecane also described as dinitrotetraoxa-diazaisowurzitane and often abbreviated as TEX, DTIW, TOIW, or DNTD is unambiguously identified by its CAS-No [130919–56–1]. It is the second most dense nitramine with an ambient temperature density of $\rho = 1.985 \text{ g cm}^{-3}$, an oxygen value of $\Omega = -42.7\%$ (Table 1). Its enthalpy of for-

Table 1. General properties of TEX.

Property	Unit	TEX
Sum formula		$\text{C}_6\text{H}_6\text{N}_4\text{O}_8$
CAS-No		[130919-56-1]
Molecular weight, m_r	g mol^{-1}	262.136
Oxygen balance, Ω	wt-%	–42.7
Density, ρ	g cm^{-3}	1.985
Enthalpy of formation, $\Delta_f H$	kJ mol^{-1}	–541
Enthalpy of explosion, $\Delta_{\text{ex}} H$	kJ mol^{-1}	1777
Enthalpy of combustion, $\Delta_{\text{comb}} H$	kJ mol^{-1}	2772
Decomposition temperature, T_{onset}	$^{\circ}\text{C}$	282
No Go Friction Force (BAM)	N	> 353
No Go Impact Energy (BAM)	J	23–25

mation has been determined experimentally to $\Delta_f H = -445 \text{ kJ mol}^{-1}$ [53]. Calculations at B3LYP 6-31 + G** level of theory yield a close value for $\Delta_f H = -448 \text{ kJ mol}^{-1}$ and assign a strain energy of 63 kJ mol^{-1} to the isowurzitane cage, which contributes to the overall energy content [74]. TEX is commercially available from ATK/USA, Explosia/Czech Republic, and Rafael/Israel.

3 Synthesis and Formation Mechanism

All synthetic routes for TEX developed so far require the nitrolysis of a hexasubstituted piperazyl derivative. Though various substituent patterns on the piperazine ring are feasible, the 1,4-diformyl-2,3,5,6-tetrahydropiperazine (DFTHP) (2) has the significant advantage in that it can be prepared through basis catalyzed condensation (Figure 3) of cheap glyoxal hydrate (20 EUR per L) and formamide (26 EUR per kg), which favors industrial scale up. The synthesis of DFTHP and its derivatives have been described in the literature [16–19]. Matyáš et al. have revisited the synthesis of DFTHP recently and have achieved yields in the 80% range using triethylamine as the base in a molar range between 0.1–0.2 mol per mole formamide [20].

Boyer et al. have reacted a 2:1 mixture of freshly prepared DFTHP and trimeric glyoxal with concentrated sulfuric acid and subsequently nitric acid (Figure 4a). Crash precipitation from ice afforded TEX as colorless crystals [12]. However numerous attempts to repeat their synthesis to

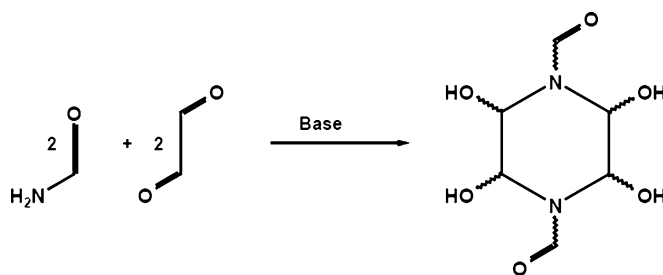


Figure 3. Synthesis of the precursor DFTHP (2).

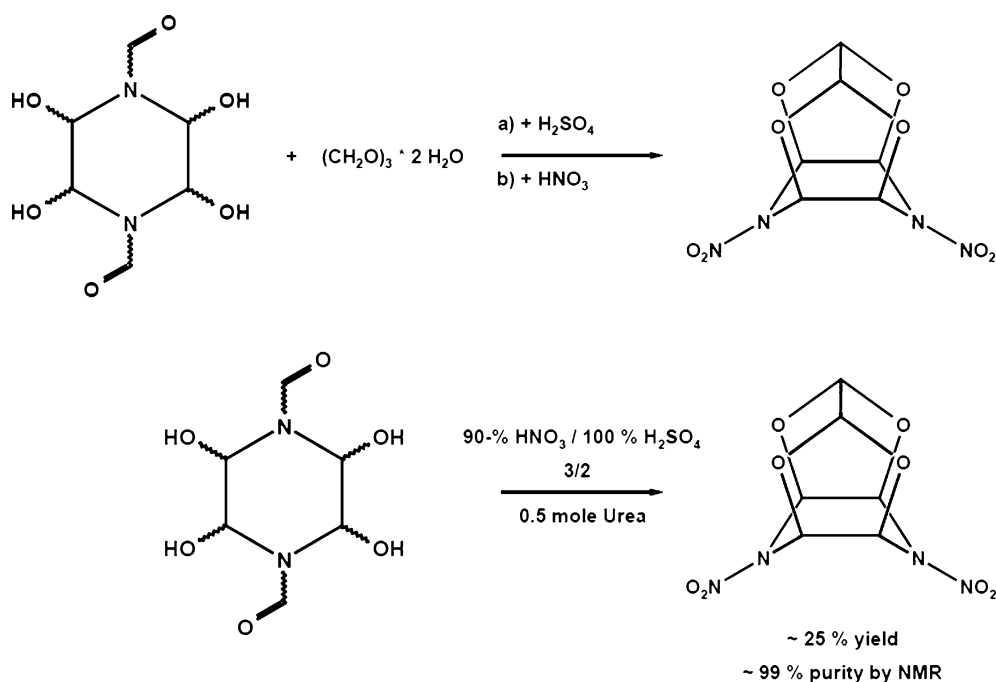


Figure 4. (above) TEX synthesis according to Boyer et al. [12]. (below) TEX synthesis according to Highsmith et al. [21].

obtain the asserted 92% yield were unsuccessful and often gave a yield < 20% with the glyoxal trimer being the main constituent of the solid precipitate [21].

The influence of the glyoxal/DFTHP ratio on the TEX synthesis was investigated by Jalový and Matyáš. They found only slight influence of glyoxal/DFTHP ratio on the yield of TEX and found that TEX also forms in absence of any glyoxal [22].

Though in the original report [12] the addition of glyoxal is described as a prerequisite for formation of TEX, Highsmith et al. prior to Ref. [22] found that formation of TEX occurs directly from DFTHP through exposure to nitrating agent [21]. Therefore a mixture of DFTHP and urea (1/0.5 mol) is added to a water cooled nitration agent made from white fuming nitric acid (WFNA) and concentrated sulfuric acid (3/2 vol-%) in the temperature range below 50 °C (Figure 4b). Heating to 65 °C and subsequent cooling af-

fords raw TEX that has to be washed with aqueous NaHCO_3 , water and methanol to remove the acid traces. To further improve the yield of TEX the same authors have suggested to pre-treat the DFTHP/urea mixtures and to add them to a nitration medium heated to temperatures between 55–70 °C [23]. A further improvement of the TEX synthesis by the same authors requires a more delicate temperature regime to be kept and the omission of urea as NO_x scavenger (Table 2) [24].

Highsmith and co-workers have investigated the formation mechanism [25].

It was found that with increasing ratio between DFTHP and nitric acid the formation time of TEX decreased until it approached 1:8. Currently it is assumed that the nitration of DFTHP gives the tetranitrate DFTNP (3) in the first reaction step (Figure 5). This is supported by the observation that reaction of DFTNP with sulfuric acid yields TEX –

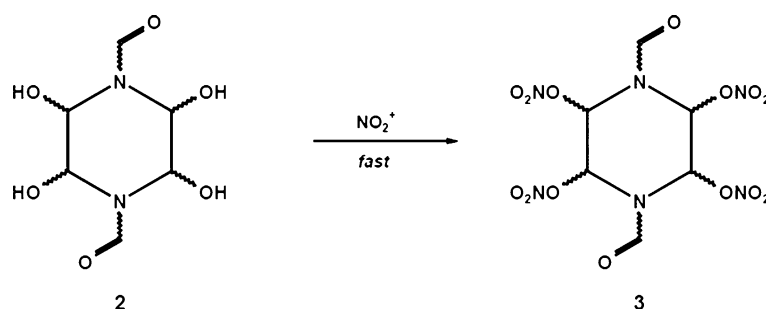


Figure 5. Formation of 1,4-diformyl-2,3,5,6-tetranitratopiperazine (3).

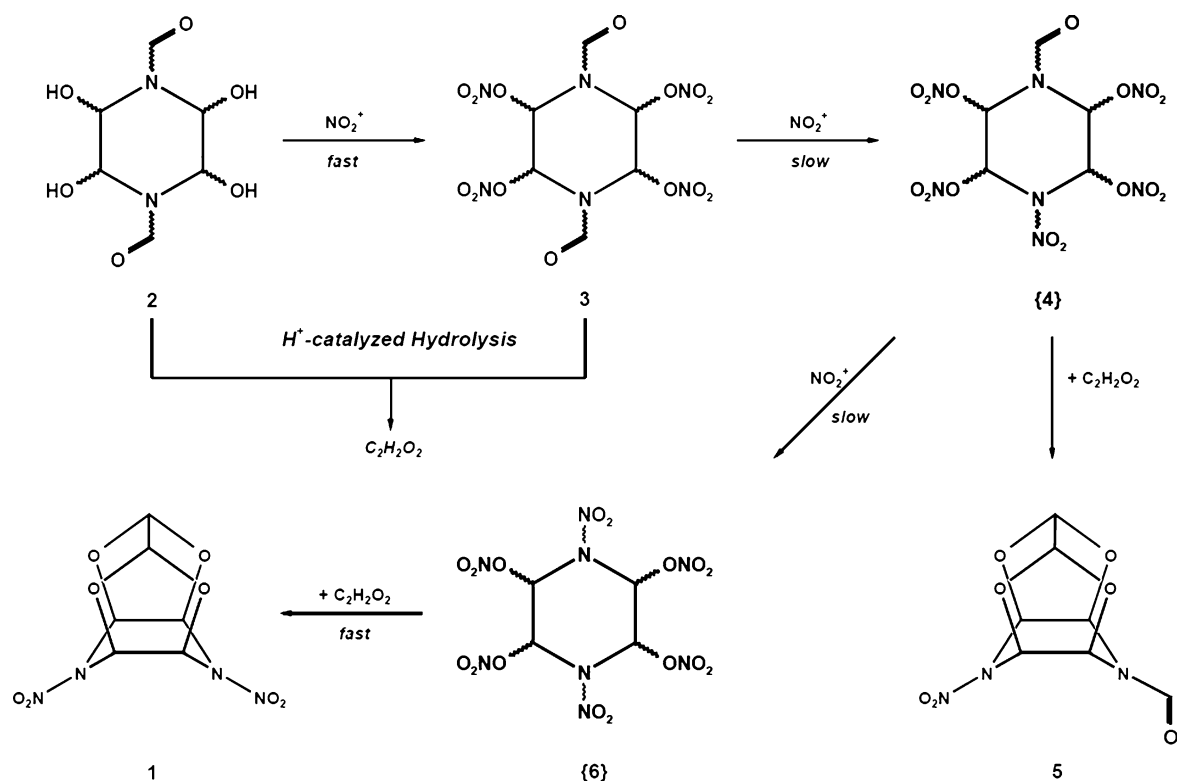


Figure 6. Assumed overall reaction path for TEX.

though in low yield [25]. **3** can also be obtained as the sole product from the reaction of DFTHP with ammonium nitrate and trifluoroacetic anhydride (TFAA) – at unknown molar ratio – [25] and has been independently characterized as the only reaction product in high yield (92%) from DFTHP with 100% nitric acid in the presence of TFAA at a DFTHP/nitric acid molar ratio of 1:4.5 [26].

1,4-Diformyl-2,3,5,6-tetranitratopiperazine (**3**) had also been obtained earlier from the reaction of 1,4-diformyl-2,3,5,6-tetrachloropiperazine and silver nitrate, AgNO_3 [17,19]. It should be noted that solid 1,4-diformyl-2,3,5,6-tetranitratopiperazine (**3**) is very sensitive to shock, friction, and impact and has been once proposed as a primary explosive [19,26].

Further reaction of **3** in solution yields the intermediate 1,4-dinitramino-2,3,5,6-tetranitropiperazine **6**, which finally reacts with a glyoxal moiety under abstraction of NO_2 to give TEX (Figure 6). The identification of 4-formyl-10-nitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (**5**) as a side product indicates the stepwise and slow nitration of **3** via intermediate **4** (Figure 6).

The yield according to the disclosed process [24,25] is between 20 and 30% by weight of DFTHP. In a disclosure for large scale production by Gottlieb et al. a yield of ca. 30% by weight of DFTHP is claimed [27].

Matyáš et al. have investigated the influence of both $\text{H}_2\text{SO}_4/\text{HNO}_3$ and DFTHP/acid ratio. They found the highest

TEX yield 37% at $\text{H}_2\text{SO}_4/\text{HNO}_3 = 0.15$ and DFTHP/acid = 66.6 ratios [20].

In a detailed study Maksimovski and Golofit have identified the optimum range for TEX synthesis based on nitrolysis of DFTHP with mixed acid. According to their findings the optimum reaction temperature is between 54 and 56 °C, with slow addition of reactants over 2 h afforded TEX in yields up to 40%. Recrystallization of TEX from fuming nitric acid yields purities > 99.5% based on ^1H NMR spectroscopy [28]. Meng et al. revisited the synthesis of TEX recently and found an overall yield of 40% when starting from glyoxal and formamide [29]. A synthetic approach to TEX using clay-supported iron(III) nitrate (*clayfeng*) instead of nitric acid has been developed by Ang and Damodaran. Reaction of DFTHP with glyoxal in the presence of *clayfeng* in 1,2-dichloroethane at ambient temperature yields 49% TEX [30]. Yet an alternative route to TEX with unprecedented high yields has been disclosed by Bayat and Azizkhani [31]. They investigated a series of heteropolylacids as heterogeneous catalysts in the nitration of DFTHP/urea mixtures and found $\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4]$ to give yields in excess of 60% at a 0.1 mmol scale of preparation. The reaction of tetrahydroxypiperazine-1,4-disulfonate salts (Li, Na, K, Cs, NH_4) with nitric acid affords TEX in yields up to 31% using the di-potassium salt [11]. According to Maksimovski et al. TEX is also observed as a major product (21% yield) in the nitration of pentanitroacetylisorwurtzitan in the presence of

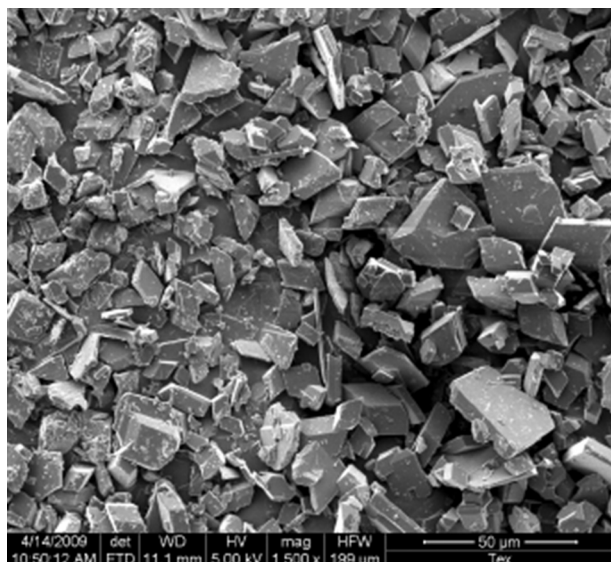


Figure 7. Electron micrograph of rough sharp TEX particles as obtained from the synthesis in Ref. [33].

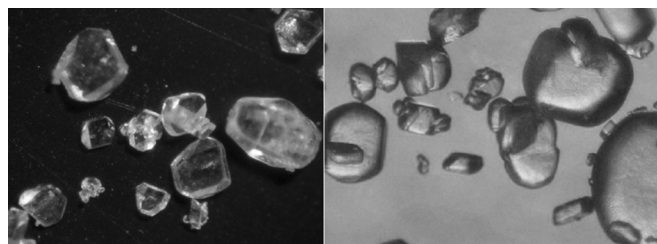


Figure 8. Optical micrograph of smooth polyedric (left) and spheroidal (right) recrystallized material from DMSO/glycerol after Refs. [34, 35].

acetic acid anhydride. Further it also occurs in the nitration of tetraacetyldibenzylhexaazaisowurzitane as trace product (1–1.4 wt-%) [32]. Particles as obtained from the process according to Ref. [33] are depicted in Figure 7.

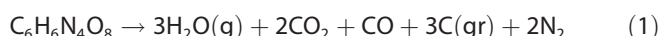
The particle engineering of TEX has been studied by Orzechowski et al. They found that crude TEX recrystallizes from DMSO and DMSO/glycerine (antisolvent) mixtures to give spheroidal crystals with high bulk densities, which are most suitable for use in explosive compositions [34, 35] (Figure 8).

4 Detonative Properties

4.1 Pure TEX

The detonative performance of TEX has been calculated with a number of codes such as BKW, Cheetah 1.36, Cheetah 2.0, EXPLO 5.0, TIGER and the Kamlet Jacobs method and are displayed in Table 2.

According to the Kamlet Jacobs method [36], the number M and N can be determined assuming a detonative reaction according to the ideal Equation (1).



$$\Delta_{\text{det}}H = -4481.1 \text{ J g}^{-1}$$

$$M = 28.26375 \text{ g mol}^{-1}$$

$$N = 0.030523 \text{ mol g}^{-1}$$

Based on calculations at different levels TEX appears to be slightly superior to nitrotriazolone (NTO) (ca. 110%) but significantly weaker than RDX (ca. 83%). Experimental determination of its performance was carried out on mixtures containing a small amount of hydrocarbon wax [41]. The results in Table 3 indicate that TEX/Wax (97/3) exhibits a critical diameter of 60 mm in the unconfined state (Figure 9). A 25 mm diameter charge with a slightly lower TEX content confined by a copper tube sustains detonation, whereas an unconfined sample of that diameter fails to propagate the shock. The position of the data in Figure 10 indicates that TEX belongs to “Group 1 explosives” as introduced by Price, which show an increase of detonation velocity as density approaches TMD [42].

Comparison of experimentally determined detonation velocity with calculated (Cheetah 2.0) value at largest diameter for TEX/Wax (97/3) and observed TMD calls for an overestimation of the detonation velocity (ca. 104%), whereas the detonation pressure is largely underestimated (ca. 91%). It however appears the TIGER code is more accurately predicting the detonation pressure.

4.2 TEX-Based Formulations

In view of its high density TEX is an interesting ingredient in IM-formulations replacing NTO but also RDX. Table 4 displays calculated data on both TEX/TNT and NTO/TNT and also compares with experimental data on NTO/TNT (*Onta-*

Table 2. Explosive performance of pure TEX as calculated with different codes and methods compared with NTO and RDX.

		BKW	Cheetah 1.36	Cheetah 2.0	Cheetah 3.0	EXPLO 5.0	TIGER	Kamlet Jacobs	NTO Cheetah 2.0	RDX Cheetah 2.0
Ref.		[14]	[37]	[38]	[33]	[39]	[40]	[36]	[38]	[38]
TMD, ρ	g cm^{-3}	1.985	1.985	1.985	1.985	1.985	1.985	1.985	1.910	1.806
V_d	m s^{-1}	8749	8160	8540	8683	8314	8665	8170	8250	9000
P_{CJ}	GPa	36.5	31.4	32.24	–	29.92	37.0	31.4	28.60	33.78
T_{CJ}	K	1706	3226	3190	–	2972	–	–	3358	4154
$V/V_0 = 2.20$	kJ cm^{-3}	–	–5.59	–5.95	–	–	–	–	–5.41	–7.16

Table 3. Results from detonation-measurements of TEX/wax formulations.

Charge diameter [mm]	Charge density [g cm ⁻³]	TMD [%]	V _d (exp.) [m s ⁻¹]	V _d (calcd.) ^{a)} [m s ⁻¹]	P _{CJ} (exp.) [GPa]	P _{CJ} (calcd.) [GPa]	Gurney velocity [m s ⁻¹]	Wax and composition ^{c)}
21	1.836	95.2	6028 ^{a)}	–	–	–	–	97 % TEX/3 % Svit 3RV® 6
30	1.825	94.7	6948	–	–	–	–	– 6
40	1.835	95.2	7298	–	–	–	–	– 6
50	1.825	94.7	7402	–	–	–	–	– 6
60	1.815	94.1	7446	–	–	–	–	– 6
95	1.802	93.5	7441	7744 ^{a)}	–	24.35 ^{a)}	–	– 6
25 ^{c)}	1.87	97.5	7075	7988 ^{a)}	29.2	26.61 ^{a)}	2510	96.5 % TEX/ 3.5 wt-% Is- 7 coblend®
				7894 ^{b)}				

Table 4. Calculated explosive performance of TEX/TNT composites and comparison with NTO/TNT.

Formulation	Unit	Calcd.	Calcd.	Calcd.	Calcd.	Exp.
Code		TIGER	Cheetah 2.0	Cheetah 2.0	Cheetah 2.0	n.a.
Ref.		[40]	[38]	[38]	[38]	[43]
Composition		TEX/TNT	TEX/TNT	TEX/TNT	NTO/TNT	NTO/TNT
		75/25	75/25	60/40	60/40	60/40 Ontalite
ρ	g cm^{-3}	1.89	1.89	1.82	1.78	1.78
TMD	%	100	100	98.96	98.96	98.96
V_d	m s^{-1}	8306	8165	7885	7751	7427
P_{CJ}	GPa	32.9	28.76	26.17	24.57	–
T_{CJ}	K	–	3333	3424	3529	–
$V/V_0=2.2$		–	–5.51	–5.17	–4.93	–
$V/V_0=6.5$	kJ cm^{-3}	–	–6.99	–6.64	–6.37	–

Table 5. (a) Compositions of various TEX based formulations [73] and comparative explosives /wt-%. (b) Composition of various TEX based formulations [72] and comparative explosives/wt-%.

(a) Ingredients	1	2	3	4	5	6	7	8	9	10
PGN	14.19	14.19	14.19	14.19	14.19	14.19	17.03	2.838	17.03	17.03
DEGDN	8.0	8.0	8.0	8.0	8.0	8.0	9.6	1.6	9.6	9.6
Desmodur® N-100	2.0	2.0	2.0	2.0	2.0	2.0	2.4	0.4	2.4	2.4
Modifiers	0.81	0.81	0.81	0.81	0.81	0.81	0.97	9.162	0.97	0.97
AP, 200 μm	27.5	26.0	25.0	27.5	27.5	27.5	–	–	–	–
Al, 15 μm	27.5	29.0	30.0	27.5	27.5	27.5	–	–	–	–
TEX, 200 μm	20.0	–	–	–	15.0	10.0	70	95	–	–
RDX	–	–	–	–	–	–	–	–	70	–
HMX	–	20.0	–	–	5.0	10.0	–	–	–	–
CL20	–	–	20.0	–	–	–	–	–	–	–
NTO	–	–	–	20.00	–	–	–	–	–	70

(b) Ingredients	11	12	13	14	15	16	17	18	19	20	21	22
TEX	42.5	–	x	20	19	38	57	76	19	38	57	76
HMX	42.5	42.5	–	–	76	57	38	19	–	–	–	–
RDX	–	–	–	–	–	–	–	–	76	57	38	19
NTO	–	42.5	88x	–	–	–	–	–	–	–	–	–
2,4-DNAN	–	–	–	≈ 40	–	–	–	–	–	–	–	–
NiGu	–	–	–	≈ 40	–	–	–	–	–	–	–	–
PTFE	–	–	–	–	5	5	5	5	5	5	5	5
HTPB	15	15	12	–	–	–	–	–	–	–	–	–

Ref. [46]. Figure 12 displays the detonation velocity of the two RDX/TEX and HMX-series as a function of TEX content.

DLE-P031 was once a candidate formulation to replace LX-14 in the future combat system. Allegedly the formulation used the same binder system as PAX 2/A (BDNPA/F) and a HMX content of approximately 80 wt-% and a TEX content of ca. 10 wt-%. The composition was tailored to match the energy content of LX-14 (HMX/Estane 95.5/4.5) [47].

Experimental testing of TEX based formulations yields detonation velocities superior to NTO based formulations provided the charges are greater than the critical diameter.

5 Propellant Performance

The propellant properties of TEX have been investigated by Talwar et al. They calculated a specific impulse of $I_s = 220$ s (at $p = 6.86$ MPa) for the hypothetical propellant composition:

49.5 wt-% nitrocellulose
30.5 wt-% nitroglycerine
3.0 wt-% carbamate
7 wt-% DEP
10 wt-% TEX,

and a specific impulse of $I_s = 210$ s for pure TEX [14].

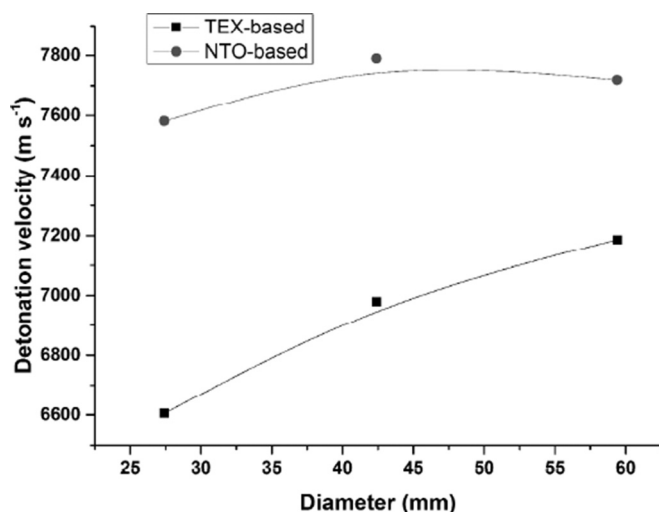
The impetus for combustible cartridge cases based on CE-BAMO/TEX has been calculated with the BLAKE code to 890 J g^{-1} [48].

Table 6. Experimental performance and comparison with Cheetah 2.0 values.

(a) Composition	Density (exp.) [g cm ⁻³]	V _d (exp.) [m s ⁻¹]	V _d (calcd.) [m s ⁻¹]	TNT-Equivalent Blast Overpressure (–)
1	?	5579		1.11
2	?	7432		
3	?	6700		
4	?			1.16
5	?			0.57
6	?			1.01
7	1.67	6811	7544	
8	1.871	7303	8135	
9	1.62	7844	8100	
10	1.47	6263	6800	

(b) Composition	Density [g cm ⁻³]	TMD [%]	Diameter [mm]	V _d (exp.) [m s ⁻¹]	V _d (calcd.) [m s ⁻¹]
11	1.635	98.73	27.4	6605	7679
11	1.635	98.73	42.4	6979	7679
11	1.635	98.73	59.4	7186	7679
12	1.620	99.19	27.4	7582	7617
12	1.620	99.19	42.4	7790	7617
12	1.620	99.19	59.4	7719	7617

a) *At TMD.

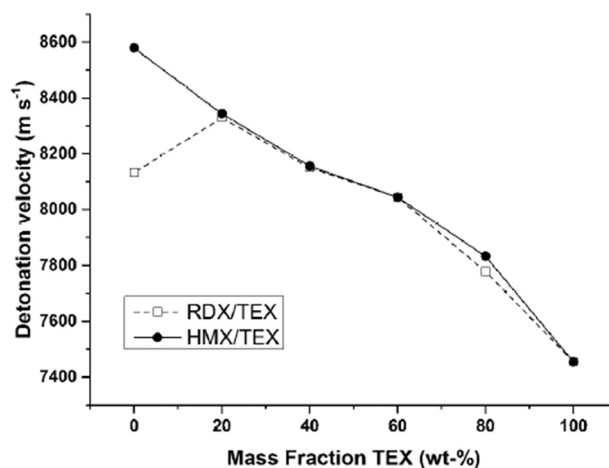

Figure 11. Detonation velocity diameter relationship after Ref. [41].

The experimental gun propellant TGD-009 bears the following composition:

58 wt-% RDX
18 wt-% TEX
6 wt-% BAMO
18 wt-% AMMO

The thermochemical properties of TGD-009 are given in Table 7.

TGD-009 has a significant lower chamber and nozzle temperature than standard propellants. However both its high CO/CO₂ and H₂/H₂O ratio cause excessive carburization


Figure 12. Detonation velocity as function of TEX mass fraction after Ref. [46].

and hydride formation and hence cause comparable gun barrel erosion as high temperature gun propellants having lower said ratios [49]. The high CO and H₂ content are due to the low oxygen balance ($\Omega = -42.7$) as compared to both RDX, and NTO which bear a higher oxygen balance [$\Omega(\text{RDX}) = -21.6\%$, $\Omega(\text{NTO}) = -24.6\%$]. Hence considering TEX as a dense an insensitive ingredient in gun propellants requires to tailoring the oxygen balance to avoid the above problems.

Given the high density, the low general sensitivity and the high oxygen content TEX could prove a useful ingredient in pyrotechnic formulations for spectral flares, which typically require a fuel with high oxygen balance [50].

Table 7. Thermochemical properties of TGD-009 as calculated with BLAKE code.

	Chamber		Nozzle			
	Temperature [K]	Force [J g^{-1}]	Temperature [K]	CO/CO ₂	H ₂ /H ₂ O	N ₂ moles/moles
TGD-009	2570	1070	1886	21.31	5.16	0.26

6 Safety and Sensitivity of TEX and its Formulations

Friction and Impact Sensitivity

TEX is not sensitive to friction ($>353\text{ N}$) [41]. The impact sensitivity for $200\text{ }\mu\text{m}$ grain sample is 33 cm with the ABL machine, $>116.8\text{ cm}$ with the proprietary Thiokol (now ATK) impact hammer [40], 42.5 cm with the NSWC/IH fallhammer [37], 50 cm with the 5 kg fallhammer [51], and 24 J with the BAM fallhammer [46].

Spark Sensitivity

The spark sensitivity of TEX of unspecified granulometry has been determined to 13.1 J [52].

Thermal Response (Cook Off)

Bulk crystalline TEX ($200\text{ }\mu\text{m}$) yields a mild (burn) response in the Simulated Bulk Auto ignition Temperature Test (SBAT) at 252°C [53]. The 5 s deflagration point has been determined to 312°C in Ref. [8]. DLE-P031 yields a partial detonation in the VCCT test at 191°C [38].

Shock Sensitivity

In the Large Scale Gap Test (LSGT) the acceptor charge is confined within a 36.5 mm internal diameter steel tube. Hence with insensitive materials failure to propagate is reduced. Table 8 shows results of TEX based formulations and some baseline formulations for comparison.

DLE-P031 has a 3.89 GPa initiation pressure with the LSGT whereas DLE-C055 has an initiation pressure of 4.36 GPa .

Table 8. Shock sensitivity according to NOL-LSGT test with TEX-based formulations and reference formulations after Ref. [40].

Formulation	Input pressure [GPa]	Test result	V_d [m s^{-1}]
1	9.2	fail	5579
1	6.98	pass	no detonation
2	9.2	fail	7432
2	6.98	fail	7180
7	21.31	fail	6811
7	6.98	pass	no detonation
8	21.31	fail	6263
8	6.98	fail	5571
9	21.31	fail	7844
9	6.98	fail	7790

Small scale water gap testing (SSWGT) has been reported for TEX containing formulations [46,51,54]. These results are however questionable in that the diameter of the samples (21 mm) is way below the critical diameter of TEX and the confinement is provided by a Plexiglas is very weak. Hence passing the test may occur just because the detonation of the test sample dies out due to too small diameter.

7 Thermal and Chemical Stability

The DSC spectrum of purified TEX displays the onset of a single exothermic event at 304°C , which has its peak at 311°C (Figure 13) [33]. There is no indication of any phase transition or fusion of TEX prior to its decomposition. However it has been and can be seen from the TGA plot that TEX sublimates at temperatures around and above 240°C [55] (Figure 13). The decomposition occurs with very little residue. The activation energy for the decomposition reaction of TEX in the solid phase has been determined to $E_A = 196.8\text{ kJ mol}^{-1}$ [56].

In the temperature range below 210°C decomposition occurs exclusively in the solid state, whereas above 240°C reactions in the gas phase take place [55].

The DSC onset for the decomposition of DLE-C055 is observed at 233°C [44].

TEX is compatible with a large number of inert and energetic binders including PGN/DEGN/Desmodur® N-100 [40]. It is further compatible with diethylenetriamine trinitrate (DET), ethylene diamine dinitrate (EDDN), nitrotriazolone

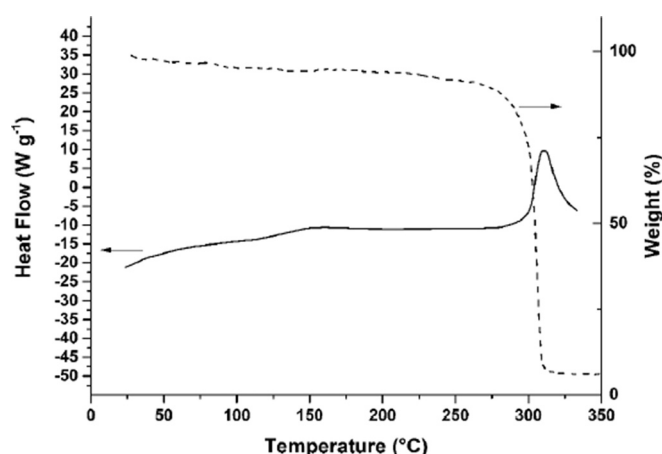
**Figure 13.** DSC and TGA spectrum of purified TEX at 10 K min^{-1} after Ref. [33].

Table 9. DSC onset for selected energetic materials and their 1:1 mixtures with TEX.

Material	Exotherm-onset [°C]	Peak [°C]	DT onset [°C]	DT peak [°C]
TEX	304	308		
NTO	274	277		
NQ	250	255		
GUDN	222	226		
RDX	219	248		
NC	203	214		
NG	187	204		
NTO/TEX	260	267	−14	−10
NQ/TEX	245	251	−5	−4
GUDN/TEX	220	223	−2	−3
RDX/TEX	222	250	+3	+2
NC/TEX	203	214	0	0
NG/TEX	181	201	−6	−3

(NTO), guanylurea dinitramide (GUDN), cyclonite (RDX), octogen (HMX), nitrocellulose (NC), nitroguanidine (NQ) and nitroglycerine (NG) [33] and glycidyl azide polymer (GAP) [57] as is evident from the DSC data in Table 9.

Türker et al. theoretically studied the hydroperoxide-formation of TEX recently and have showed this to be a spontaneous process [58]. According to their work hydroperoxide formation does neither significantly alter the sensitivity nor the performance of TEX.

Vacuum Stability

TEX passes vacuum stability testing at 110 °C for 20 h with 0.05 mLg^{−1} [54] and 0.05 mLg^{−1} at 100 °C after 48 h [40]. DLE-P031 passes the vacuum stability test with 0.2 mLg^{−1} (48 h @ 100 °C)[47]. Two formulations, (CL-20/TEX/HTPB 32/48/20) and (HMX/TEX/HTPB 32/48/20) yield 0.44 mLg^{−1} (20 h @ 100 °C) and 0.04 mLg^{−1} (20 h @ 100 °C), respectively [51].

8 Structural and Crystallographic Data

So far the structure of TEX has been investigated in four independent studies [10,59–61]. The highest crystallographic density of 2.03 g cm^{−3} was determined at 100 K [59].

In relation to CL-20 the bond lengths and bond angles are typical for an isowurzitane cage compound (Table 10, Table 11). The designation pattern is given in Figure 14. The crystallographic designations follow the nomenclature as indicated in Figure 2. The molecular packing of TEX is close to a distorted hexagonal close packing of spheres. The crystal lattice contains two differently oriented TEX molecules. The intermolecular O...H–C distances are between 239–256 pm which is similar to those found in other dense nitramines. The bond length for the N4–N13 is significantly smaller than a single bond (1.39–1.41 pm) but still larger than a typical N=N double bond (1.20).

Table 10. Crystallographic data of TEX as determined in two independent studies [59,60].

	Unit	Ref. [60]	Ref. [59]
Density	g cm ^{−3}	2.008	2.03
Temperature	K	200	100
Crystal system		triclinic	triclinic
Space group		<i>P</i> 1	<i>P</i> 1
<i>Z</i>		2	2
<i>a</i>	Å	6.8360(12)	6.814(1)
<i>b</i>	Å	7.6404(14)	7.622(1)
<i>c</i>	Å	8.7765(16)	8.733(1)
α	°	82.37(2)	82.23(1)
β	°	75.05(2)	75.02(1)
γ	°	79.46(2)	79.45(1)
<i>V</i>	Å ³	433.64(14)	428.8(1)
Reflexes used		1911	2240
<i>wR</i>		0.099	0.055
<i>R</i>		0.034	0.033
$\Delta\rho_{\max}$	e Å ^{−3}	0.25	0.42
$\Delta\rho_{\min}$	e Å ^{−3}	−0.25	−0.31

Table 11. Selected bond lengths [pm] of TEX from Refs. [61,62].

	Ref. [62]	Ref. [61]
C1–C7	1.577(2)	1.579(1)
C1–O2	1.4222(16)	1.414(1)
O2–C3	1.4222(17)	1.417(2)
C3–N4	1.450(2)	1.451(1)
C3–C11	1.5628(19)	1.555(1)
N4–C5	1.4672(18)	1.449(1)
N4–N13	1.4162(16)	1.394(1)
N13–O14	1.2139(19)	1.226(1)
N13–O15	1.218(2)	1.214(1)
C5–C9	1.5574(19)	1.562(1)

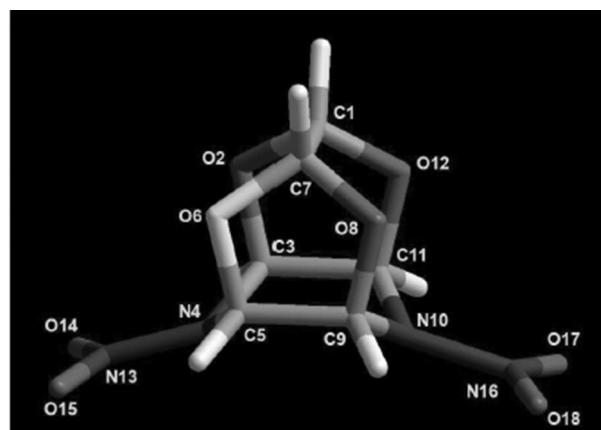


Figure 14. Crystallographic designation of atoms in TEX.

The influence of hydrostatic pressure in the range between 0–100 GPa on the structural, electronic and optical properties of TEX have been studied at DFT level of theory by Liu et al. [62].

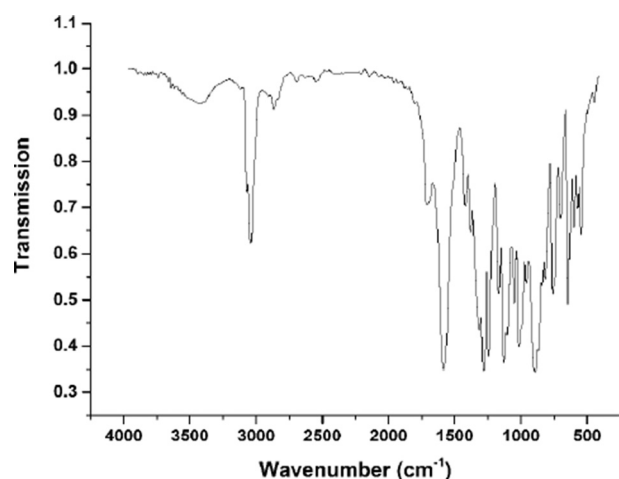


Figure 15. FT-IR spectrum of TEX after Ref. [63].

Table 12. FT-IR wavenumbers and assignments of TEX.

Assignment	ν [cm^{-1}]
C–H	3051
N–NO ₂	1591 (s) 1429 1388
N–NO ₂	1287 (s) 1251 1174
C–O–C	1136 (s) 1056 1022 966 899 (s) 823 766 708 651 607 578 553

9 Spectroscopic Information

Vibrational Spectroscopy

A typical FT-IR spectrum of TEX is displayed in Figure 15 the important vibrational bands (cm^{-1}) of which are listed in Table 12.

NMR Spectroscopy

Thanks to its high symmetry TEX yields only few signals with no measurable coupling. In Table 13 the chemical shifts for ^1H , ^{13}C , and ^{15}N NMR spectra are given.

Mass Spectroscopy

Denekamp and Tsoglin have investigated the MS spectrum of TEX in detail [64]. Unlike CL-20 they found that TEX does not form any attachment ions in the chemical ionization mode. Methane positive chemical ionization ($\text{CH}_4\text{-PCI}$) yields the MH^+ ion $m/z=263$ (RA 100%) and a signal at $m/s=188$ that may be due to loss of HNO_2 and CO (RA 19%), there is an $[\text{MH}-\text{HNO}_2]^+$ ion at m/z 216 (RA 16%). Boyer investigated the mass spectrum with undisclosed ionization technique affording a distinct signal for the $\text{M}^+ - \text{NO}_2$ peak. The 100% peak is due to glyoxal fragment but no molecule ion peak.

10 Miscellaneous

Klapötke et al. investigated the thermochemistry of hypothetical dinitramide salts of TEX at B3LYP/6-31 + G(d,p) level of theory [65]. Recently Türker has performed a number of extensive DFT-level calculations on susceptibility of TEX to undergo protonation [66] and decomposition upon irradiation with α -particles [67]. Türker also studied possible nitrogen analogues of TEX [71].

Toxicity and Environmental Impact

Relevant for considering the environmental impact of TEX is its solubility in water. This has been determined to 27 mg l^{-1} , which is in the same ballpark as the solubility of RDX (33 mg l^{-1}). Likewise its effect on the fathead minnow

Table 13. NMR shifts of TEX from Refs. [21, 22, 76].

Designation	^1H [D ₆]acetone	^1H (300 MHz) [D ₆]DMSO	^{13}C [D ₆]acetone	^{13}C (75 MHz) [D ₆]DMSO	^{15}N
H-1, H-7	5.95 (s), 2 H	5.95 (s), 2 H			
H-3, H-5, H-9, H-11	7.08 (s), 4 H	7.08 (s), 2 H			
C-1, C-7			102.65	102.65	
C-3, C-5, C-9, C-11			82.68	82.63	
N-NO ₂ -4, N-NO ₂ -10					–33.40
N-NO ₂ -4, N-NO ₂ -10					–197.20

(*Pimephales promelas*) is comparable to that of RDX [45]. The cytotoxicity on mice splenocytes, CL₅₀ (TEX) is identical to HMX and significantly lower than RDX [68]. Its enzymatic reduction through PETN reductase occurs faster than with RDX [69].

The vapor pressure of TEX at ambient temperature is 9.39×10^{-7} Pa, which is lower than RDX (2.10×10^{-6} Pa) but still orders of magnitude larger than HMX ($p = 2.08 \times 10^{-11}$ Pa) [70].

11 Conclusions and Outlook

TEX is the second most dense nitramine explosive [$\rho(20^\circ\text{C}) = 1.985 \text{ g cm}^{-3}$] following CL-20. However unlike CL-20, TEX is friction insensitive, possesses low impact sensitivity (ca. 24 J with BAM Impact tester) and exhibits a very large critical diameter ≥ 60 mm that makes this energetic material suitable for large charges such as general purpose bombs or torpedo warheads. TEX bears a very low shock sensitivity in the NOL-LSGT (50% $p > 6.98$ GPa) and possesses excellent compatibility with a wide range of binders and other energetic materials. TEX is synthesized in ca. 40% overall yield from inexpensive starting materials in a straightforward process. Its production does not require any specialized equipment and the associated waste stream (neutralized spent acid) is non-hazardous. Given its advantageous IM properties and the low cost of its starting materials, TEX merits consideration for large scale use in appropriate formulations.

Acknowledgments

The author gratefully acknowledges Professor Thomas M. Klapötke, Ludwig Maximilian Universität Munich, Germany for carrying out EXPLO 5.0 calculations and Dr. Andrzej Orzechowski, Institute of Industrial Organic Chemistry Warzaw, Poland for kind permission to reproduce optical micrographs of recrystallized TEX crystals.

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Received: August 14, 2014

Revised: September 26, 2014

Published online: November 21, 2014