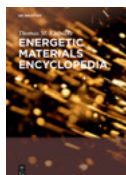


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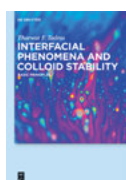
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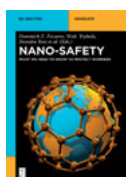
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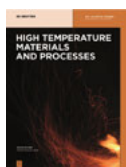
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Thomas M. Klapötke

Chemistry of High-Energy Materials

3rd Edition

DE GRUYTER

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ISBN 978-3-11-043932-8
e-ISBN (PDF) 978-3-11-043933-5
e-ISBN (EPUB) 978-3-11-043047-9

Library of Congress Cataloging-in-Publication Data

A CIP catalog record for this book has been applied for at the Library of Congress.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie;
detailed bibliographic data are available on the Internet at <http://dnb.dnb.de>.

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Cover image: Fischer Test $\text{Pb}(\text{N}_3)_2$; provided by Prof. Klapötke

Typesetting: Meta Systems Publishing & Printservices GmbH, Wustermark

Printing and binding: CPI books GmbH, Leck

☼ Printed on acid-free paper

Printed in Germany

www.degruyter.com

“We will not waver; we will not tire; we will not falter; and we will not fail.
Peace and freedom will prevail.”

G. W. Bush, Presidential Address to the Nation,
October 7th 2001

Preface to this 3rd English edition

Everything which has been said in the preface to the first German and first and second English editions still holds and essentially does not need any addition or correction. In this revised third edition in English the manuscript has been updated and various recent aspects of energetic materials have been added:

- (i) some errors which unfortunately occurred in the first and second editions have been corrected and the references have also been updated where appropriate.
- (ii) The chapters on critical diameters, delay compositions, visible light (blue) pyrotechnics, polymer-bonded explosives (PBX), HNS, thermodynamic calculations, DNAN, smoke (yellow) formulations and high-nitrogen compounds have been updated.
- (iii) Five new short chapters on Ignition and Initiation (chapters 5.2 and 5.3), the Plate Dent Test (chapter 7.4), Underwater Explosions (chapter 7.5) and the Trauzl Test (chapter 6.6) have been added.

In addition to the people thanked in the German and first and second English editions, the author would like to thank Dr. Vladimir Golubev and Tomasz Witkowski (both LMU) for many inspired discussions concerning hydrocode calculations. The author is also indebted to and thanks Dr. Manuel Joas (DynITEC, Troisdorf, Germany) for his help with the preparation of chapters 5.2 and 5.3.

Munich, October 2015

Thomas M. Klapötke

Preface to this 2nd English edition

Everything said in the preface to the first German and first English editions still holds and essentially does not need any addition or correction. In this revised second edition in English we have up-dated the manuscript and added some recent aspects of energetic materials:

- (i) We have tried to correct some mistakes which can not be avoided in a first edition and also updated the references where appropriate.
- (ii) The chapters on Ionic Liquids, Primary Explosives, NIR formulations, Smoke Compositions and High-Nitrogen Compounds were updated.
- (iii) Two new short chapters on Co-Crystallization (9.5) and Future Energetic Materials (9.6) have been added.

In addition to the people thanked in the German and first English edition, the author would like to thank Dr. Jesse Sabatini and Dr. Karl Oyler (ARDEC, Picatinny Arsenal, NJ) for many inspired discussions concerning pyrotechnics.

Munich, May 2012

Thomas M. Klapötke

Preface to the first English edition

Everything said in the preface to the first German edition remains valid and essentially does not need any addition or correction. There are several reasons for translating this book into English:

- The corresponding lecture series at LMU is now given in English in the post-graduate M.Sc. classes, to account for the growing number of foreign students and also to familiarize German students with the English technical terms.
- To make the book available to a larger readership world-wide.
- To provide a basis for the author's lecture series at the University of Maryland, College Park.

We have tried to correct some omissions and errors which can not be avoided in a first edition and have also updated the references where appropriate. In addition, five new chapters on Combustion (Ch. 1.4), NIR formulations (Ch. 2.5.5), the Gurney Model (Ch. 7.3), dinitroguanidine chemistry (Ch. 9.4) and nanothermites (Ch. 13.3) have been included in the English edition. The chapter on calculated combustion parameters (Ch. 4.2.3) has been extended.

In addition to the people thanked in the German edition, the author would like to thank Dr. Ernst-Christian Koch (NATO, MSIAC, Brussels) for pointing out various mistakes and inconsistencies in the first German edition. For inspired discussions concerning the Gurney model special thanks goes to Joe Backofen (BRIGS Co., Oak Hill). Dr. Anthony Bellamy, Dr. Michael Cartwright (Cranfield University), Neha Mehta, Dr. Reddy Damavarapu and Gary Chen (ARDEC) and Dr. Jörg Stierstorfer (LMU) are thanked for ongoing discussions concerning secondary and primary explosives.

The author also thanks Mr. Davin Piercey, B.Sc. for corrections and for writing the new chapter on nanothermites, Dr. Christiane Rotter for her help preparing the English figures and Dr. Xaver Steemann for his help with the chapter on detonation theory and the new combustion chapter. The author thanks the staff of de Gruyter for the good collaboration preparing the final manuscript.

Munich, January 2011

Thomas M. Klapötke

Preface to the first German edition

This book is based on a lecture course which has been given by the author for more than 10 years at the Ludwig-Maximilian University Munich (LMU) in the post-graduate Master lecture series, to introduce the reader to the chemistry of highly energetic materials. This book also reflects the research interests of the author. It was decided to entitle the book “Chemistry of High-Energy Materials” and not simply “Chemistry of Explosives” because we also wanted to include pyrotechnics, propellant charges and rocket propellants into the discussion. On purpose we do not give a comprehensive historical overview and we also refrained from extensive mathematical deductions. Instead we want to focus on the basics of chemical explosives and we want to provide an overview of recent developments in the research of energetic materials.

This book is concerned with both the civil applications of high-energy materials (e.g. propellants for carrier or satellite launch rockets and satellite propulsion systems) as well as the many military aspects. In the latter area there have been many challenges for energetic materials scientists in recent days some of which are listed below:

- In contrast to classical targets, in the on-going global war on terror (GWT), new targets such as tunnels, caves and remote desert or mountain areas have become important.
- The efficient and immediate response to time critical targets (targets that move) has become increasingly important for an effective defense strategy.
- Particularly important is the increased precision (“we want to hit and not to miss the target”, Adam Cumming, DSTL, Sevenoaks, U.K.), in order to avoid collateral damage as much as possible. In this context, an effective coupling with the target is essential. This is particularly important since some evil regimes often purposely co-localize military targets with civilian centers (e.g. military bases near hospitals or settlements).
- The interest in insensitive munitions (IM) is still one of the biggest and most important challenges in the research of new highly energetic materials.
- The large area of increasing the survivability (for example by introducing smokeless propellants and propellant charges, reduced signatures of rocket motors and last but not least, by increasing the energy density) is another vast area of huge challenge for modern synthetic chemistry.
- Last but not least, ecological aspects have become more and more important. For example, on-going research is trying to find suitable lead-free primary explosives in order to replace lead azide and lead styphnate in primary compositions. Moreover, RDX shows significant eco- and human-toxicity and research is underway to find suitable alternatives for this widely used high explosive. Finally, in the area of rocket propulsion and pyrotechnical compositions, replacements for toxic ammonium perchlorate (replaces iodide in the thyroid

gland) which is currently used as an oxidizer are urgently needed. Despite all this, the performance and sensitivity of a high-energy material are almost always the key-factors that determine the application of such materials – and exactly this makes research in this area a great challenge for synthetically oriented chemists.

The most important aspect of this book and the corresponding lecture series at LMU Munich, is to prevent and stop the already on-going loss of experience, knowledge and know-how in the area of the synthesis and safe handling of highly energetic compounds. There is an on-going demand in society for safe and reliable propellants, propellant charges, pyrotechnics and explosives in both the military and civilian sector. And there is no one better suited to provide this expertise than well trained and educated preparative chemists.

Last but not least, the author wants to thank those who have helped to make this book project a success. For many inspired discussions and suggestions the authors wants to thank the following colleagues and friends: Dr. Betsy M. Rice, Dr. Brad Forch and Dr. Ed Byrd (US Army Research Laboratory, Aberdeen, MD), Prof. Dr. Manfred Held (EADS, TDW, Schrobenhausen), Dr. Ernst-Christian Koch (NATO MSIAC, Brussels), Dr. Miloslav Krupka (OZM, Czech Republic), Dr. Muhamed Suceca (Brodarski Institute, Zagreb, Croatia), Prof. Dr. Konstantin Karaghiosoff (LMU Munich), Prof. Dr. Jürgen Evers (LMU Munich), as well as many of the past and present co-workers of the authors research group in Munich without their help this project could not have been completed.

The author is also indebted to and thanks Dipl.-Chem. Norbert Mayr (LMU Munich) for his support with many hard- and soft-ware problems, Ms. Carmen Nowak and Ms. Irene S. Scheckenbach (LMU Munich) for generating many figures and for reading a difficult manuscript. The author particularly wants to thank Dr. Stephanie Dawson (de Gruyter) for the excellent and efficient collaboration.

Munich, July 2009

Thomas M. Klapötke

Contents

Preface to this 3rd English edition — vii

Preface to this 2nd English edition — viii

Preface to the first English edition — ix

Preface to the first German edition — x

1 Introduction — 1

- 1.1 Historical Overview — 1
- 1.2 New Developments — 10
 - 1.2.1 Polymer-Bonded Explosives — 10
 - 1.2.2 New High (Secondary) Explosives — 13
 - 1.2.3 New Primary Explosives — 23
 - 1.2.4 New Oxidizers for Solid Rocket Motors — 32
- 1.3 Definitions — 35
- 1.4 Combustion, Deflagration, Detonation – A Short Introduction — 39
 - 1.4.1 Fire and Combustion — 39
 - 1.4.2 Deflagration and Detonation — 42

2 Classification of Energetic Materials — 45

- 2.1 Primary Explosives — 45
- 2.2 High (Secondary) Explosives — 48
- 2.3 Propellant Charges — 55
- 2.4 Rocket Propellants — 58
- 2.4.1 Chemical Thermal Propulsion (CTP) — 69
- 2.5 Pyrotechnics — 70
 - 2.5.1 Detonators, Initiators, Delay Compositions and Heat-Generating Pyrotechnics — 70
 - 2.5.2 Light-Generating Pyrotechnics — 74
 - 2.5.3 Decoy Flares — 81
 - 2.5.4 Smoke Munitions — 87
 - 2.5.5 Near-Infrared (NIR) Compositions — 96

3 Detonation, Detonation Velocity and Detonation Pressure — 99

4 Thermodynamics — 107

- 4.1 Theoretical Basis — 107
- 4.2 Computational Methods — 113
 - 4.2.1 Thermodynamics — 113

4.2.2	Detonation Parameters —	116
4.2.3	Combustion Parameters —	121
4.2.4	Example: Theoretical Evaluation of New Solid Rocket Propellants —	126
4.2.5	Example: EXPLO5 Calculation of the Gun Propellant Properties of Single, Double and Triple Base Propellants —	133
5	Initiation —	137
5.1	Introduction —	137
5.2	Ignition and Initiation of Energetic Materials —	139
5.3	Laser Ignition and Initiation —	141
6	Experimental Characterization of Explosives —	149
6.1	Sensitivities —	149
6.2	Long-Term Stabilities —	154
6.3	Insensitive Munitions —	156
6.4	Gap Test —	158
6.5	Classification —	159
6.6	Trauzl Test —	161
7	Special Aspects of Explosives —	165
7.1	Shaped Charges —	165
7.2	Detonation Velocities —	171
7.3	Gurney Model —	177
7.3.1	Example: Calculation of the Gurney Velocity for a General Purpose Bomb —	181
7.4	Plate Dent Tests vs. Fragment Velocities —	182
7.5	Underwater explosions —	189
8	Correlation between the Electrostatic Potential and the Impact Sensitivity —	195
8.1	Electrostatic Potentials —	195
8.2	Volume-Based Sensitivities —	198
9	Design of Novel Energetic Materials —	201
9.1	Classification —	201
9.2	Polynitrogen Compounds —	203
9.3	High-Nitrogen Compounds —	208
9.3.1	Tetrazole and Dinitramide Chemistry —	209
9.3.2	Tetrazole, Tetrazine and Trinitroethyl Chemistry —	216
9.3.3	Ionic Liquids —	221
9.4	Dinitroguanidine Derivatives —	225

9.5	Co-Crystallization — 227
9.6	Future Energetics — 228
10	Synthesis of Energetic Materials — 237
10.1	Molecular Building Blocks — 237
10.2	Nitration Reactions — 238
10.3	Processing — 243
11	Safe Handling of Energetic Materials in the Laboratory — 245
11.1	General — 245
11.2	Protective Equipment — 246
11.3	Laboratory Equipment — 249
12	Energetic Materials of the Future — 251
13	Related Topics — 259
13.1	Thermobaric Weapons — 259
13.2	Agent Defeat Weapons — 261
13.3	Nanothermites — 263
13.3.1	Example: Iron Oxide / Aluminum Thermite — 269
13.3.2	Example: Copper Oxide / Aluminum Thermite — 271
13.3.3	Example: Molybdenum Trioxide / Aluminum Thermite — 272
13.4	Homemade Explosives — 272
14	Study Questions — 273
15	Literature — 277
16	Appendix — 287
	Important reaction types in organic nitrogen chemistry — 287
	Curing of a diol (HTPB) with isocyanate binder — 291
	Important reaction types in inorganic nitrogen chemistry — 291
	Collection of formulas — 301
Author — 307	
Index — 309	

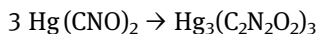
1 Introduction

1.1 Historical Overview

In this chapter we do not want to be exhaustive in scope, but rather to focus on some of the most important milestones in the chemistry of explosives (Tab. 1.1). The development of energetic materials began with the accidental discovery of **blackpowder** in China (~ 220 BC). In Europe this important discovery remained dormant until the 13th and 14th centuries, when the English monk Roger Bacon (1249) and the German monk Berthold Schwarz (1320) started to research the properties of blackpowder. At the end of the 13th century, blackpowder was finally introduced into the military world. However, it was not until 1425 that Corning greatly improved the production methods and blackpowder (or gunpowder) was then introduced as a propellant charge for smaller and later also for large calibre guns.

The next milestone was the first small-scale synthesis of **nitroglycerine (NG)** by the Italian chemist Ascanio Sobrero (1846). Later, in 1863 Imanuel Nobel and his son Alfred commercialized NG production in a small factory near Stockholm (Tab. 1.1). NG is produced by running highly concentrated, almost anhydrous, and nearly chemically pure glycerine into a highly concentrated mixture of nitric and sulfuric acids ($\text{HNO}_3 / \text{H}_2\text{SO}_4$), while cooling and stirring the mixture efficiently. At the end of the reaction, the nitroglycerine and acid mixture is transferred into a separator, where the NG is separated by gravity. Afterwards, washing processes using water and alkaline soda solution remove any residual acid.

Initially NG was very difficult to handle because of its high impact sensitivity and unreliable initiation by blackpowder. Among many other accidents, one explosion in 1864 destroyed the Nobel factory completely, killing Alfred's brother Emil. In the same year, Alfred Nobel invented the metal blasting cap detonator, and replaced blackpowder with **mercury fulminate (MF)**, $\text{Hg}(\text{CNO})_2$. Although the Swedish-German Scientist Johann Kunkel von Löwenstern had described $\text{Hg}(\text{CNO})_2$ as far back as in the 17th century, it did not have any practical application prior to Alfred Nobel's blasting caps. It is interesting to mention that it was not until the year 2007 that the molecular structure of $\text{Hg}(\text{CNO})_2$ was elucidated by the LMU research team (Fig. 1.1) [1, 2]. Literature also reports the thermal transformation of MF, which, according to the below equation, forms a new mercury containing explosive product which is reported to be stable up to 120 °C.



After another devastating explosion in 1866 which completely destroyed the NG factory, Alfred Nobel focused on the safe handling of NG explosives. In order to reduce the sensitivity, Nobel mixed NG (75 %) with an absorbent clay called "Kieselguhr" (25 %). This mixture called "Guhr Dynamite" was patented in 1867. Despite

Tab. 1.1: Historical overview of some important secondary explosives.

substance	acronym	development	application	density/g cm ⁻³	explosive power ^b
blackpowder	BP	1250–1320	1425–1900	ca. 1.0	
nitroglycerine	NG	1863	in propellant charges	1.60	170
dynamite	Dy	1867	civil/commercial only	varies	varies
picric acid	PA	1885–1888	WW I	1.77	100
nitroguanidine	NQ	1877	most in TLPs	1.71	99
trinitrotoluene	TNT	1880	WW I	1.64	116
nitropenta	PETN	1894	WW II	1.77	167
hexogen	RDX	1920–1940	WW II	1.81	169
octogen	HMX	1943	WW II	1.91	169
hexanitrostilbene	HNS	1913	1966	(β polymorph) 1.74	
triaminotrinitrobenzene	TATB	1888	1978	1.93	
HNIW	CL-20	1987	under evaluation	2.1	
				(ϵ polymorph)	

^a rel. to PA

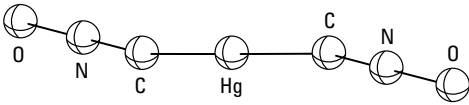


Fig. 1.1: Molecular structure of mercury fulminate, $\text{Hg}(\text{CNO})_2$.

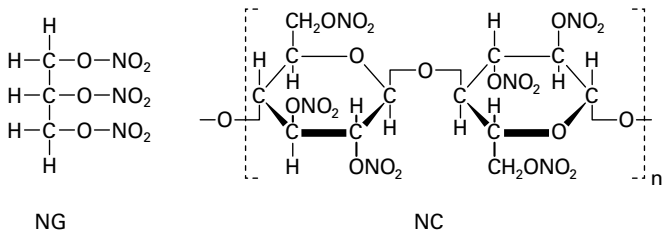


Fig. 1.2: Molecular structures of nitroglycerine (NG) and nitrocellulose (NC).

the great success of dynamite in the civil sector, this formulation has never found significant application or use in the military sector.

One of the great advantages of NG (Fig. 1.2) in comparison to blackpowder (75 % KNO_3 , 10 % S_8 , 15 % charcoal) is that it contains both the fuel and oxidizer in the same molecule which guarantees optimal contact between both components,

whereas in blackpowder, the oxidizer (KNO_3) and the fuel (S_8 , charcoal) have to be physically mixed.

At the same time as NG was being researched and formulated several other research groups (Schönbein, Basel and Böttger, Frankfurt-am-Main) worked on the nitration of cellulose to produce **nitrocellulose (NC)**. In 1875 Alfred Nobel discovered that when NC is formulated with NG, they form a gel. This gel was further refined to produce blasting gelatine, gelatine dynamite and later in 1888 ballistite (49% NC, 49% NG, 2% benzene and camphor), which was the first smokeless powder. (Cordite which was developed in 1889 in Britain, had a very similar composition.) In 1867 it was proven that mixtures of NG or dynamite and ammonium nitrate (AN) showed enhanced performance. Such mixtures were used in the civil sector. In 1950 manufacturers started to develop explosives which were waterproof and solely contained the less hazardous AN. The most prominent formulation was ANFO (Ammonium Nitrate Fuel Oil) which found extensive use in commercial areas (mining, quarries etc.). Since the 1970s aluminium and monomethylamine were added to such formulations to produce gelled explosives which could detonate more easily. More recent developments include production of emulsion explosives which contain suspended droplets of a solution of AN in oil. Such emulsions are water proof, yet readily detonate because the AN and oil are in direct contact. Generally, emulsion explosives are safer than dynamite and are simple and cheap to produce.

Picric acid (PA) was first reported in 1742 by Glauber, however it was not used as an explosive until the late 19th century (1885–1888), when it replaced blackpowder in nearly all military operations world-wide (Fig. 1.3). PA is prepared best by dissolving phenol in sulfuric acid and the subsequent nitration of the resulting of phenol-2,4-disulfonic acid with nitric acid. The direct nitration of phenol with nitric acid is not possible because the oxidizing HNO_3 decomposes the phenol molecule. Since the sulfonation is reversible, the $-\text{SO}_3\text{H}$ groups can then be replaced with $-\text{NO}_2$ groups by refluxing the disulfonic acid in concentrated nitric acid. In this step the third nitro group is introduced as well. Although pure PA can be handled safely, a disadvantage of PA is its tendency to form impact sensitive metal salts (picrates, primary explosives) when in direct contact with shell walls. PA was used as a grenade and as mine filling.

Tetryl was developed at the end of the 19th century (Fig. 1.3) and represents the first explosive of the nitroamino (short: nitramino) type. Tetryl is best obtained by dissolving monomethylaniline in sulfuric acid and then pouring the solution into nitric acid, while cooling the process.

The above mentioned disadvantages of PA are overcome by the introduction of **trinitrotoluene (TNT)**. Pure 2,4,6-TNT was first prepared by Hepp (Fig. 1.3) and its structure was determined by Claus and Becker in 1883. In the early 20th century TNT almost completely replaced PA and became the standard explosive during WW I. TNT is produced by the nitration of toluene with mixed nitric and sulfuric acid.

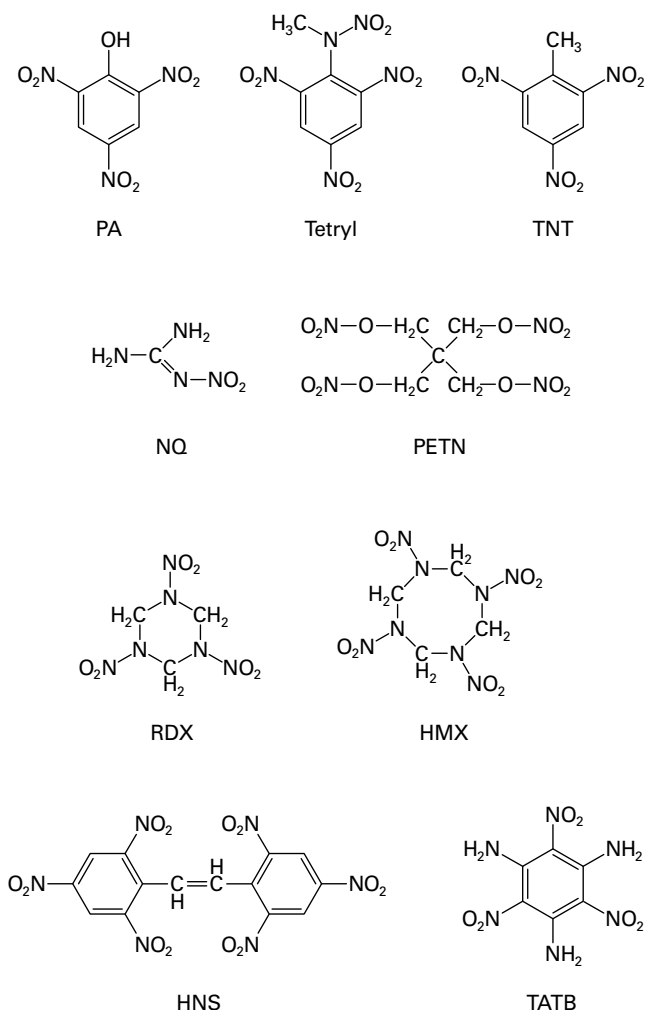
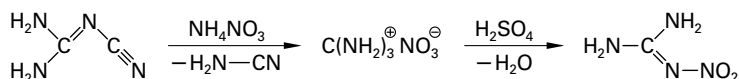


Fig. 1.3: Molecular structures of picric acid (PA), tetryl, trinitrotoluene (TNT), Nitroguanidine (NQ), pentaerythritol tetranitrate (PETN), hexogen (RDX), octogen (HMX), hexanitrostilbene (HNS) and triaminotrinitrobenzene (TATB).

For military purposes TNT must be free of any isomer other than the 2,4,6-isomer. This is achieved by recrystallization from organic solvents or from 62% nitric acid. TNT is still one of the most important explosives for blasting charges today. Charges are produced through casting and pressing. However, cast charges of TNT often show sensitivity issues and do not comply with the modern insensitive munition requirements (IM). For this reason alternatives to TNT have been suggested. One of these replacements for TNT is NTO (filler) combined with 2,4-dinitroanisole (DNAN, binder).

Nitroguanidine (NQ) was first prepared by Jousselein in 1887 (Fig. 1.3). However, during WW I and WW II it only found limited use, for example in formulations with AN in grenades for mortars. In more recent days NQ has been used as a component in triple-base propellants together with NC and NG. One advantage of the triple-base propellants is that unlike double-base propellants the muzzle flash is reduced. The introduction of about 50 % of NQ to a propellant composition also results in a reduction of the combustion temperature and consequently reduced erosion and increased lifetime of the gun. NQ can be prepared from dicyandiamide and ammonium nitrate via guanidinium nitrate which is dehydrated with sulfuric acid under the formation of NQ:



The most widely used explosives in WW II other than TNT were hexogen (RDX) and pentaerythritol tetranitrate (nitropenta, PETN) (Fig. 1.3). Since PETN is more sensitive and chemically less stable than RDX, RDX was (and is) the most commonly used high explosive. PETN is a powerful high explosive and has a great shattering effect (brisance). It is used in grenades, blasting caps, detonation cords and boosters. PETN is not used in its pure form because it is too sensitive. A formulation of 50 % TNT and 50 % PETN is known as “pentolite”. In combination with plasticized nitrocellulose PETN is used to form polymer bonded explosives (PBX). The military application of PETN has largely been replaced by RDX. PETN is prepared by introducing pentaerythritol into concentrated nitric acid while cooling and stirring the mixture efficiently. The then formed bulk of PETN crystallizes out of the acid solution. The solution is then diluted to about 70 % HNO_3 in order to precipitate the remaining product. The washed crude product is purified by recrystallization from acetone.

Hexogen (RDX) was first prepared in 1899 by Henning for medicinal use. (*N.B.* NG and PETN are also used in medicine to treat angina pectoris. The principal action of these nitrate esters is vasodilation (i.e. widening of the blood vessels). This effect arises because in the body the nitrate esters are converted to nitric oxide (NO) by mitochondrial aldehyde dehydrogenase, and nitric oxide is a natural vasodilator.) In 1920 Herz prepared RDX for the first time by the direct nitration of hexamethylene tetramine. Shortly afterwards Hale (Picatinny Arsenal, NJ) developed a process that formed RDX in 68 % yield. The two processes most widely used in WW II were

1. the Bachmann process (KA process) in which hexamethylene tetramine dinitrate reacts with AN and a small amount of nitric acid in an acetic anhydride medium to form RDX (type B RDX). The yields are high, however, 8–12 % of HMX form as a side product.
2. the Brockman process (type A RDX) essentially produces pure RDX.

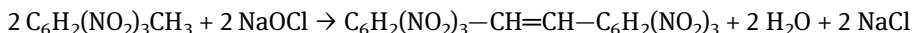
Tab. 1.2: Composition of some high explosive formulations.

name	composition
Composition A	88.3 % RDX, 11.7 % non-energetic plasticizers
Composition B	60 % RDX, 39 % TNT, 1 % binder (wax)
Composition C4	90 % RDX, 10 % polyisobutylene
octol	75 % HMX, 25 % RDX
torpex ^b	42 % RDX, 40 % TNT, 18 % aluminum
PBXN-109	64 % RDX, 20 % aluminum, 16 % binder
OKFOL	96.5 % HMX, 3.5 % wax

^a An Australian improved development of torpex is known under the name H6 and also contains hexogen (RDX), trinitrotoluene (TNT) and aluminum. H6 was used as a high explosive formulation in the MOAB bomb (Massive Ordnance Air Blast bomb). MOAB (also known as GBU-43/B) is with a load of approx. 9500 kg high explosive formulation one of the largest conventional bombs ever used.

After WW II **octogen (HMX)** started to become available. Until today, most high explosive compositions for military use are based on TNT, RDX and HMX (Tab. 1.2).

Since 1966 **hexanitrostilbene (HNS)** and since 1978 **triaminotrinitrobenzene (TATB)** are produced commercially (Fig. 1.3). Both secondary explosives show excellent thermal stabilities and are therefore of great interest for the NAVY (fuel fires) and for hot deep oil drilling applications (Fig. 1.3). Especially HNS is known as a heat- and radiation-resistant explosive which is used in heat-resistant explosives in the oil industry. The brisance of HNS is lower than that of RDX, but the melting point of approx. 320 °C is much higher. HNS can directly be prepared from trinitrotoluene through oxidation with sodium hypochlorite in a methanol/THF solution:



Since oil deposits which are located closer to the surface are becoming rare, deeper oil reserves now have to be explored where (unfortunately) higher temperatures are involved. Therefore, there is an ongoing search for explosives which are even more thermally stable (decomposition temperatures > 320 °C) than HNS, but at the same time show better performance (Tab 1.2a). Higher thermal stabilities usually result in compounds with lower sensitivities which are therefore safer to handle.

According to J. P. Agrawal, new energetic materials with high thermal stabilities can be achieved by incorporating the following points in the compounds:

- Salt formation
- Introduction of amino groups
- Introduction of conjugation
- Condensation with a triazole ring.

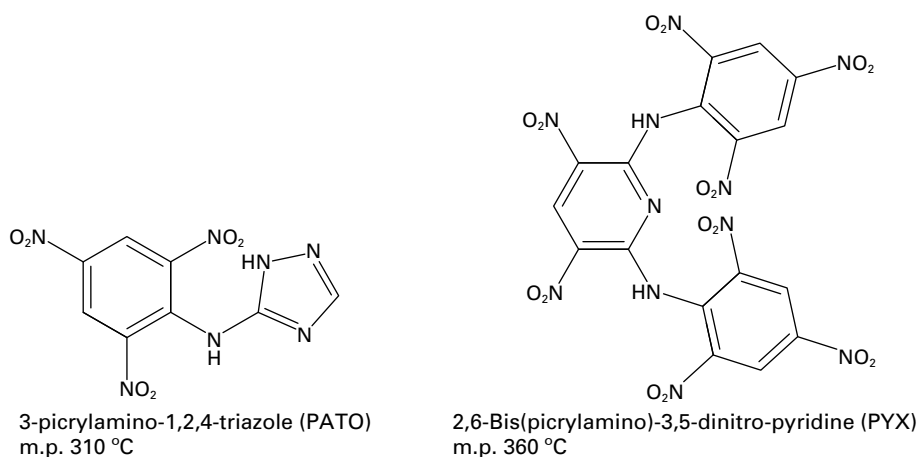
Two possible replacements for HNS which are presently under investigation are PYX and PATO.

Various picryl and picrylamino substituted 1,2,4–triazoles which were formed by condensing 1,2,4-triazole or amino-1,2,4-triazole with picryl chloride (1-chloro-

Tab. 1.2a: Desired properties of potential HNS replacements

Thermal Stability	No changes after 100 h at 260 °C
Detonation Velocity	> 7500 m/s
Specific Energy *	> 975 kJ/kg
Impact Sensitivity	> 7.4 J
Friction Sensitivity	> 235 N
Total Costs	< 500 Euro/kg
Critical diameter	≥ HNS

* specific energy. $F = p_e \cdot V = n \cdot R \cdot T$

**Fig. 1.3a:** Molecular structures of PATO and PYX.

2,4,6-trinitrobenzene) were studied in detail by Coburn & Jackson. One of these molecules is PATO (3-picrylamino-1,2,4-triazole), a well known, thermally stable explosive, which is obtained by the condensation of picryl chloride with 3-amino-1,2,4-triazole (Fig. 1.3a). Another promising candidate for a high-temperature explosive is PYX (Fig. 1.3a). The synthesis for PYX is shown in Fig. 1.3b.

Agrawal et al. reported the synthesis of BTDAONAB (Fig. 1.3c) which does not melt below 550 °C and is considered to be a better and thermally more stable explosive than TATB. According to the authors, this material has a very low impact (21 J), no friction sensitivity (> 360 N) and is thermally stable up to 550 °C. These reported properties makes BTDAONAB superior to all of the nitro-aromatic compounds which have been discussed. BTDAONAB has a VoD of 8300 m/s while TATB is about 8000 m/s [Agrawal et al., *Ind. J. Eng. & Mater Sci.*, **2004**, 11, 516–520; Agrawal et al., *Central Europ. J. Energ. Mat.* **2012**, 9(3), 273–290.]

Moreover, recently another nitro-aromatic compound (BeTDAONAB), similar to Agrawal's BTDAONAB has been published by Keshavaraz et al., which is also very

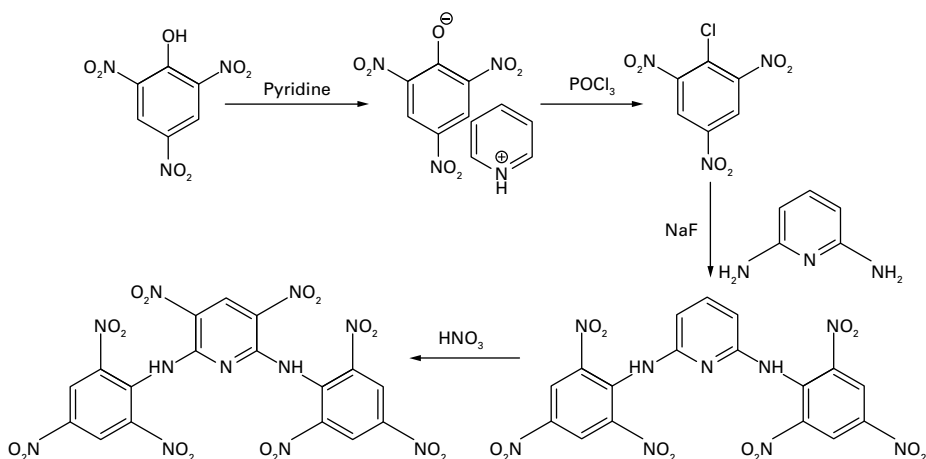


Fig. 1.3b: Synthetic route for PYX.

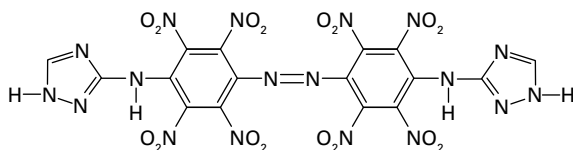


Fig. 1.3c: Molecular structure of BTDAONAB.

insensitive (Fig 1.3d). In this compound, the terminal triazole moieties have been replaced by two more energetic (more endothermic) tetrazole units [Keshavaraz et al., *Central Europ. J. Energ. Mat.* **2013**, 10(4), 455; Keshavaraz et al., *Propellants, Explos. Pyrotech.*, DOI: 10.1002/prop.201500017]. Table 1.2b shows a comparison of the thermal and explosive properties of TATB, HNS, BTDAONAB and BeTDAONAB.

Tab. 1.2b: Comparative data of the thermal and explosive properties of TATB, HNS, BTDAONAB and BeTDAONAB.

Property	TATB	HNS	BTDAONAB	BeTDAONAB
density / g/cc	1.94	1.74	1.97	1.98
Sensitivity to temperature / °C	360	318	350	260
DTA (exo) / °C	360	353	550	275
DSC (exo) / °C	371	350		268
Ω_{CO} / %	-18.6	-17.8	-6.8	-5.9
IS / J	50	5	21	21
FS / N	> 353	240	353	362
VoD / m s ⁻¹	7900	7600	8600	8700
p _{C-J} / kbar	273	244	341	354

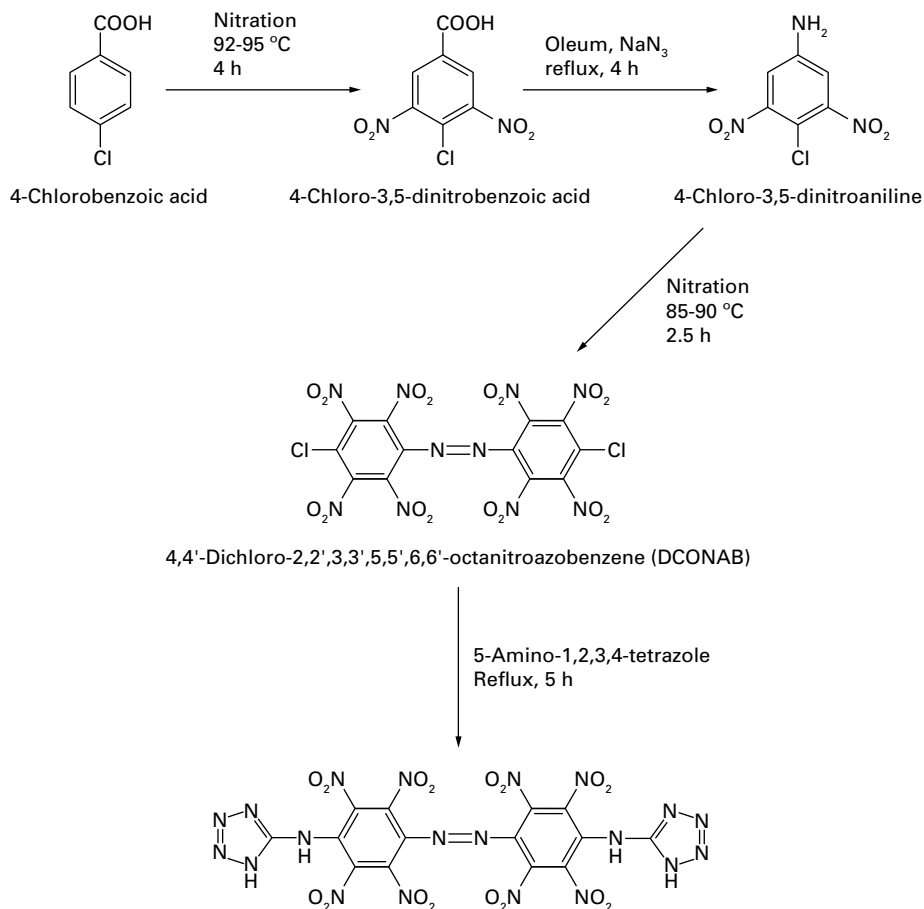


Fig. 1.3d: Synthetic route for the synthesis of BeTDAONAB.

TATB is obtained from trichloro benzene by nitration followed by a reaction of the formed trichlorotrinitro benzene with ammonia gas in benzene or xylene solution.

As shown above, the number of chemical compounds which have been used for high explosive formulations until after WW II is relatively small (Tab. 1.1 and 1.2). As we can also see from Table 1.1 and 1.2 the best performing high explosives (RDX and HMX; TNT is only used because of its melt-cast applications) possess relatively high densities and contain oxidizer (nitro and nitrate groups) and fuel (C–H backbone) combined in one and the same molecule. One of the most powerful new high explosive is **CL-20** which was first synthesized in 1987 by the Naval Air Warfare Center (NAWF) China Lake (Fig. 1.7, Tab. 1.1). CL-20 is a cage compound with significant cage strain which also contains nitramine groups as oxidizers and possesses a density of about 2 g cm⁻³. This already explains the better performance

in comparison with RDX and HMX. However, due to the relatively high sensitivity of the (desirable) ε polymorph as well as possible phase transition problems and high production costs so far CL-20's wide and general application has not been established.

1.2 New Developments

1.2.1 Polymer-Bonded Explosives

Since about 1950 polymer-bonded (or plastic-bonded) explosives (PBX) have been developed in order to reduce sensitivity and to facilitate safe and easy handling. PBX also show improved processibility and mechanical properties. In such materials the crystalline explosive is embedded in a rubber-like polymeric matrix. One of the most prominent examples of a PBX is **Semtex**. Semtex was invented in 1966 by Stanislav Brebera, a chemist who worked for VCHZ Synthesia in Semtin (hence the name Semtex), a suburb of Pardubice in the Czech Republic. Semtex consists of varying ratios of PETN and RDX. Usually polyisobutylene is used for the polymeric matrix, and phthalic acid n-octylester is the plasticizer. Other polymer matrices which have been introduced are polyurethane, polyvinyl alcohol, PTFE (teflon), Viton, Kel-F and various polyesters.

Often, however, problems can arise when combining the polar explosive (RDX) with the non-polar polymeric binder (e.g. polybutadiene or polypropylene). In order to overcome such problems, additives are used to facilitate mixing and intermolecular interactions. One of such polar additives is dantacol (DHE) (Fig. 1.4).

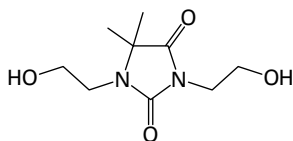


Fig. 1.4: Structure of Dantacol (DHE).

One disadvantage of the polymer-bonded explosives of the first generation, is that the non-energetic binder (polymer) and plasticizer lessened the performance. To overcome this problem energetic binders and plasticizers have been developed. The most prominent examples for **energetic binders** are (Fig. 1.5, a):

- poly-GLYN, poly(glycidyl)nitrate
- poly-NIMMO, poly(3-nitratomethyl-3-methyl-oxetane)
- GAP, glycidylazide polymer
- poly-AMMO, poly(3-azidomethyl-3-methyl-oxetane),
- poly-BAMO, poly(3,3-bis-azidomethyl-oxetane).

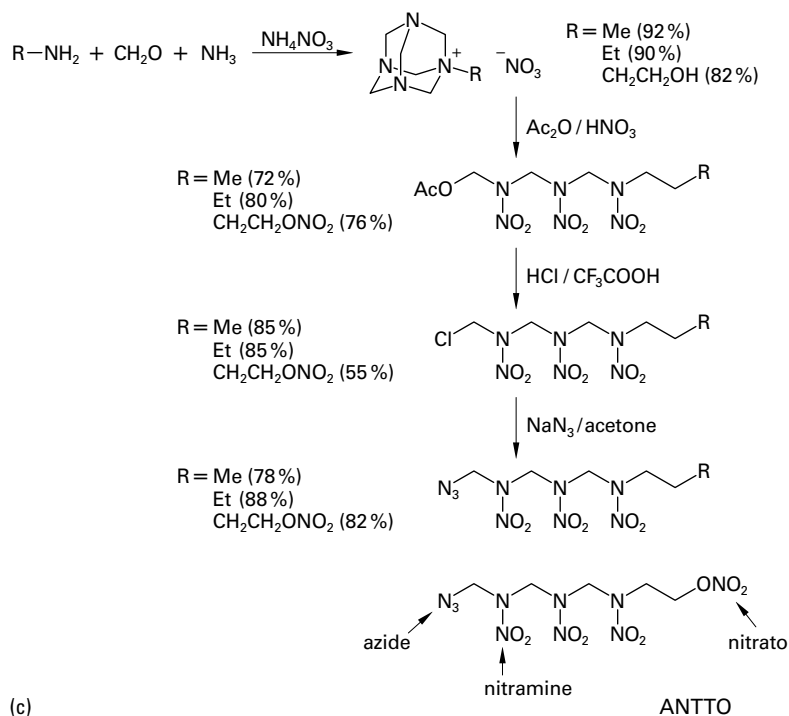
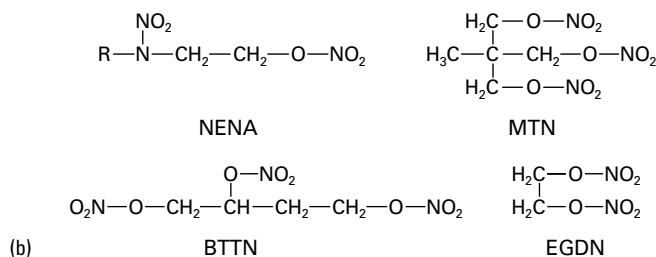
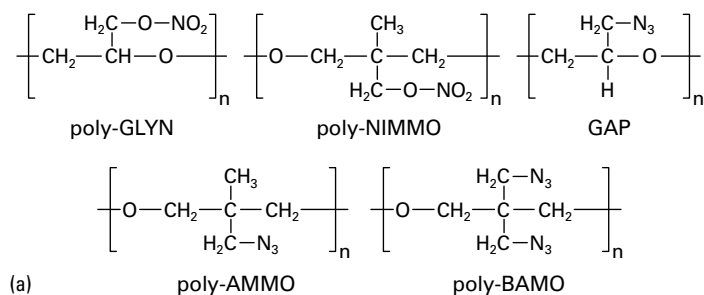


Fig. 1.5: Energetic binders (a) and energetic plasticizers (b). Synthesis of the NENA compound, ANTTO (c).

Examples for **energetic plasticizers** are (Fig. 1.5, b):

- NENA derivatives, alkylnitrateethylnitramine,
- EGDN, ethyleneglycoldinitrate,
- MTN, metrioltrinitrate,
- BTTN, butane-1,2,4-trioltrinitrate.

For binders in particular – but also for plasticizers – it is important to know the glass transition temperature. The value of the glass transition temperature should be as low as possible but at least $-50\text{ }^{\circ}\text{C}$. If the temperature of a polymer drops below T_g , it behaves in an increasingly brittle manner. As the temperature rises above T_g , the polymer becomes more rubber-like. Therefore, knowledge of T_g is essential in the selection of materials for various applications. In general, values of T_g well below room temperature correspond to elastomers and values above room temperature to rigid, structural polymers.

In a more quantitative approach for the characterization of the liquid-glass transition phenomenon and T_g , it should be noted that in cooling an amorphous material from the liquid state, there is no abrupt change in volume such as that which occurs on cooling a crystalline material below its freezing point, T_f . Instead, at the glass transition temperature, T_g , there is a change in the slope of the curve of specific volume vs. temperature, moving from a low value in the glassy state to a higher value in the rubbery state over a range of temperatures. This comparison between a crystalline material (1) and an amorphous material (2) is illustrated in the figure below. Note that the intersection of the two straight line segments of curve (2) defines the quantity T_g (Fig. 1.5a).

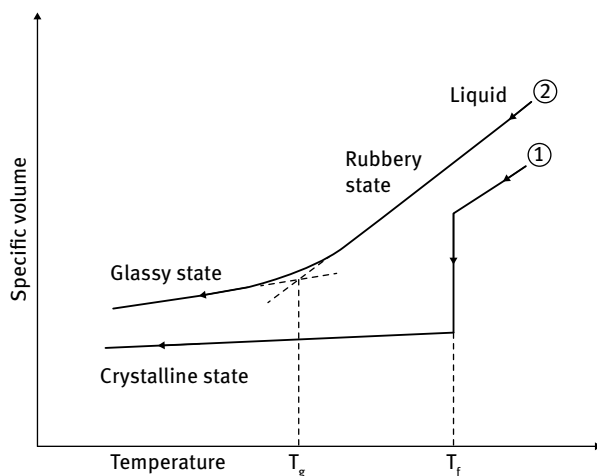


Fig. 1.5a: Specific volume vs. temperature plot for a crystalline solid and a glassy material with a glass transition temperature (T_g).

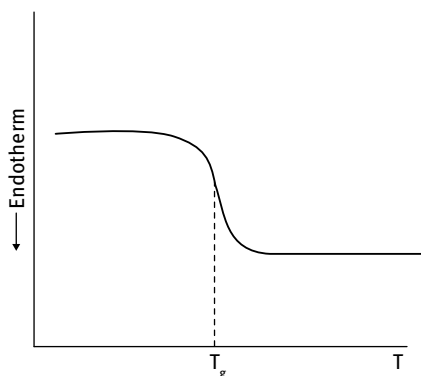
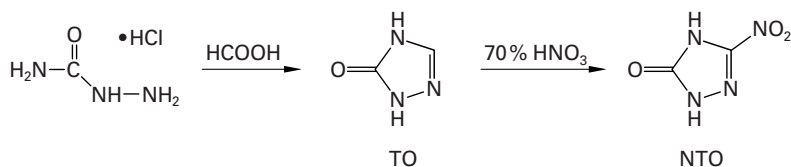


Fig. 1.5b: DSC plot illustrating the glass transition process for a glassy polymer which does not crystallize and is being slowly heated from below T_g .

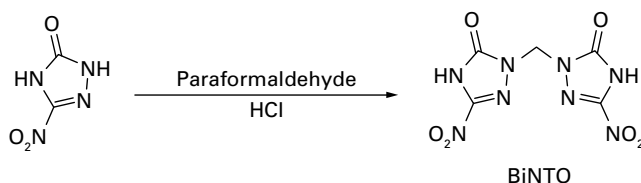
Differential scanning calorimetry (DSC) can be used to determine experimentally the glass transition temperature. The glass transition process is illustrated in Fig. 1.5b for a glassy polymer which does not crystallize and is being slowly heated from a temperature below T_g . Here, the drop which is marked T_g at its midpoint, represents the increase in energy which is supplied to the sample to maintain it at the same temperature as the reference material. This is necessary due to the relatively rapid increase in the heat capacity of the sample as its temperature increases pass T_g . The addition of heat energy corresponds to the endothermal direction.

1.2.2 New High (Secondary) Explosives

New secondary explosives which are currently under research, development or testing include 5-nitro-1,2,4-triazol-3-one (NTO), 1,3,3-trinitroazetidine (TNAZ), hexanitrohexaazaisowurtzitane (HNIW, CL-20) and octanitrocubane (ONC) (Fig. 1.7). **NTO** has already found application as a very insensitive compound in gas generators for automobile inflatable air bags and in some polymer-bonded explosive formulations. (*N.B.* Initially NaN_3 was used in air bag systems, however, nowadays guanidinium nitrate is often used in combination with oxidizers such as AN in some non-azide automotive inflators. It is used to enhance burning at low flame temperatures. Low flame temperatures are desired in order to reduce the formation of NO_x gasses in inflators.) NTO is usually produced in a two-step process from semicarbazide hydrochloride with formic acid via the intermediate formation of 1,2,4-triazol-5-one (TO) and subsequent nitration with 70 % nitric acid:



Another interesting new and neutral high explosive is BiNTO, which can be synthesized as shown in the below equation from commercially available NTO in a one-step reaction.



TNAZ was first synthesized in 1983 and has a strained four-membered ring backbone with both C-nitro and nitramine (N—NO₂) functionalities. There are various routes that yield TNAZ all of which consist of several reaction steps. One possible synthesis of TNAZ is shown in Figure 1.6. It starts from epichlorohydrin and 'Bu-amine. As far as the author of this book is aware, there has been no wide-spread use for TNAZ so far.

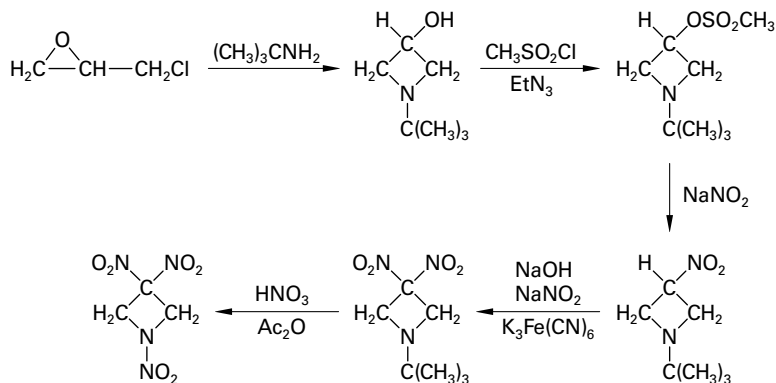


Fig. 1.6: Synthesis of 1,3,3-trinitroazetidine (TNAZ).

CL-20 (1987, A. Nielsen) and ONC (1997, Eaton) are without doubt the most prominent recent explosives based on molecules with considerable cage-strain. While CL-20 is now already produced in 100 kg quantities (e.g. by SNPE, France or Thiokol, USA, ca. \$ 1000.-/2b) on industrial pilot scale plants, ONC is only avail-

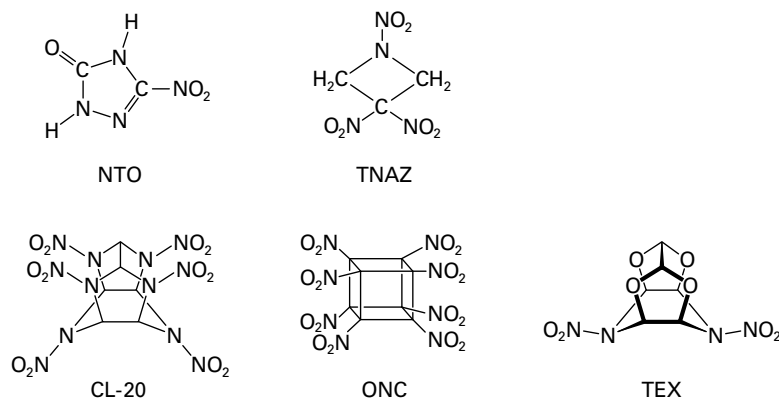


Fig. 1.7: Molecular structures of 5-nitro-1,2,4-triazol-3-one (NTO), 1,3,3-trinitroazetidine (TNAZ), hexanitrohexaazaisowurtzitane (CL-20), octanitrocubane (ONC) and 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaaisowurtzitane (TEX).

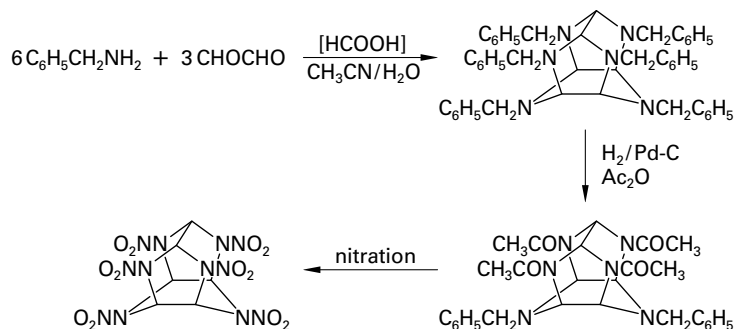


Fig. 1.8: Synthesis of hexanitrohexaazaisowurtzitane (CL-20).

able on a mg to g scale because of its very difficult synthesis. Despite the great enthusiasm for CL-20 since its discovery over 20 years ago it has to be mentioned that even today most of the high explosive formulations are based on RDX (see Tab. 1.2). There are several reasons why CL-20 despite its great performance has not yet been introduced successfully:

- CL-20 is much more expensive than the relatively cheap RDX.
- CL-20 has some sensitivity issues (see insensitive munitions).
- CL-20 exists in several polymorphic forms and the desired ϵ polymorph (because of its high density and detonation velocity) is thermodynamically not the most stable one.

Interconversion of the ϵ form into a more stable but perhaps also more sensitive other polymorph would result in a loss of performance and an increase in sensitivity.

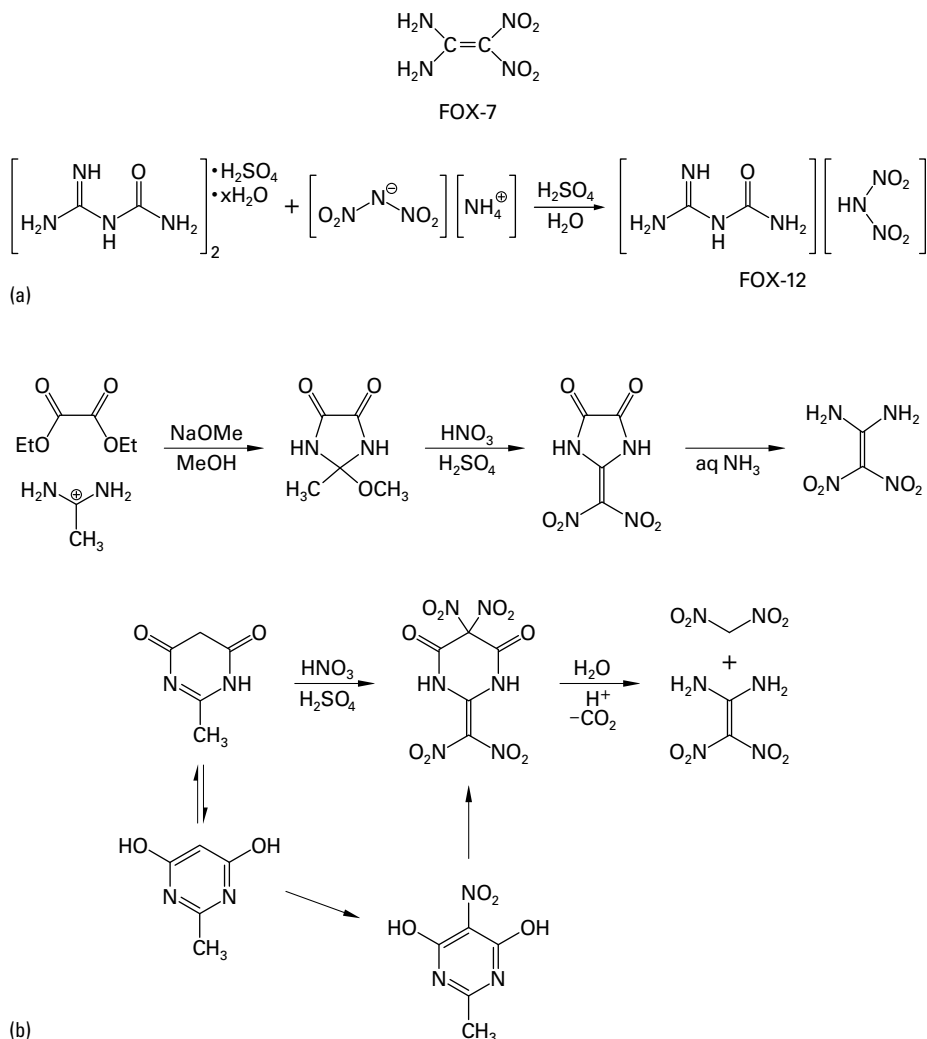


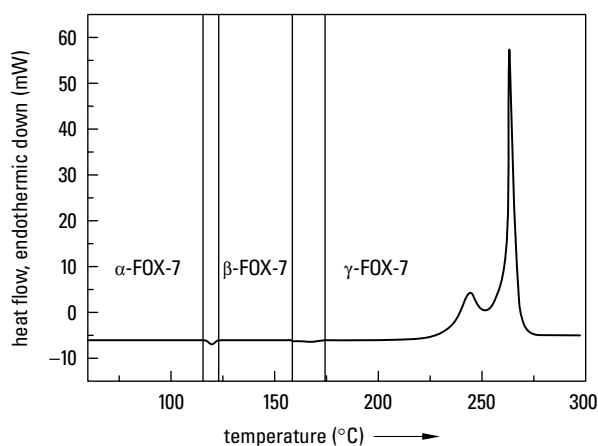
Fig. 1.9: Molecular structures of FOX-7 and FOX-12 (a). Two alternative synthetic routes for the synthesis of FOX-7 (b).

CL-20 is obtained by the condensation of glyoxal with benzylamine in an acid catalyzed reaction to yield hexabenzylhexaazaisowurtzitane (Fig. 1.8). Afterwards the benzyl groups are replaced under reducing conditions (Pd-C catalyst) by easily removable acetyl substituents. Nitration to form CL-20 takes place in the final reaction step.

Another very insensitive high explosive which is structurally closely related to CL-20 is 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (**TEX**, see Fig. 1.7), which was first described by Ramakrishnan and his co-workers in 1990. It displays one of the highest densities of all nitramines (2.008 g cm^{-3}) [1c].

Tab. 1.3: Characteristic performance and sensitivity data of FOX-7 and FOX-12 in comparison with RDX.

	FOX-7	FOX-12	RDX
detonation pressure, p_{C-J} / kbar	340	260	347
detonation velocity, D / $m\ s^{-1}$	8870	7900	8750
impact sensitivity / J	25	> 90	7.5
friction sensitivity / N	> 350	> 352	120
ESD / J	ca. 4.5	> 3	0.2

**Fig. 1.10:** DSC-Plot of FOX-7.

The chemist N. Latypov of the Swedish defense agency FOI developed and synthesized two other new energetic materials. These two compounds have become known as **FOX-7** and **FOX-12** (Fig. 1.9, a). FOX-7 or DADNE (diamino dinitro ethene) is the covalent molecule 1,1-diamino-2,2-dinitro ethene: $(O_2N)_2C=C(NH_2)_2$. The synthesis of FOX-7 always includes several reaction steps. Two alternative ways to prepare FOX-7 are shown in Figure 1.9 (b). FOX-12 or GUDN (guanylurea dinitramide) is the dinitramide of guanylurea: $[H_2N-C(=NH_2)-NH-C(O)-NH_2]^+[N(NO_2)_2]^-$.

It is interesting that FOX-7 has the same C/H/N/O ratio as RDX or HMX. Although neither FOX-7 nor (and in particular not) FOX-12 meet RDX in terms of performance (detonation velocity and detonation pressure). Both compounds are much less sensitive than RDX and might be of interest due to their insensitive munition (IM) properties. Table 1.3 shows the most characteristic performance and sensitivity data of FOX-7 and FOX-12 in comparison with RDX.

FOX-7 exists in at least three different polymorphic forms (α , β and γ). The α modification converts reversibly into the β form at 389 K (Fig. 1.10) [2]. At 435 K the β polymorph converts into the γ phase and this interconversion is not reversi-

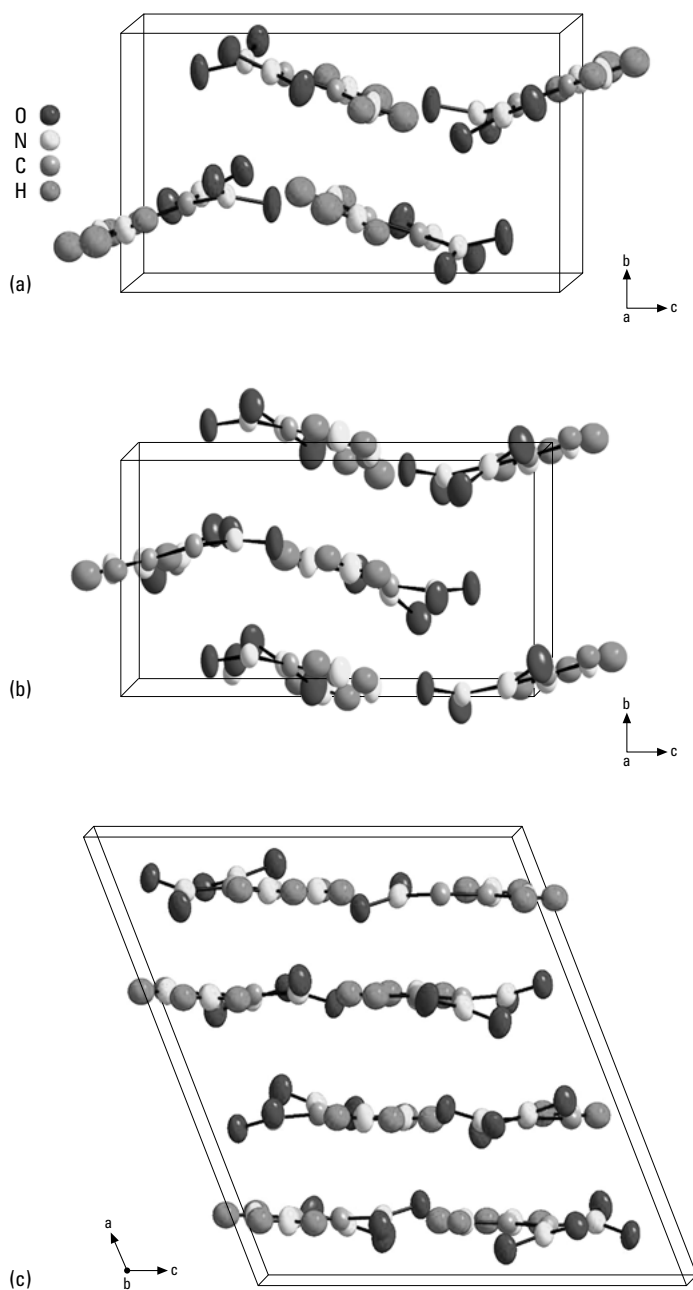


Fig. 1.11: Crystalline packing of α -FOX-7 (a), β -FOX-7 (b) and γ -FOX-7 (c).