

# Emerging Energetic Materials: Synthesis, Physicochemical, and Detonation Properties

Dabir S. Viswanath · Tushar K. Ghosh  
Veera M. Boddu

# Emerging Energetic Materials: Synthesis, Physicochemical, and Detonation Properties

 Springer

Dabir S. Viswanath  
Nuclear Science and Engineering Institute  
University of Missouri  
Columbia, MO  
USA

and

Nuclear Engineering Teaching Laboratory  
Cockrell School of Engineering  
Austin, TX  
USA

Tushar K. Ghosh  
Nuclear Science and Engineering Institute  
University of Missouri  
Columbia, MO  
USA

Veera M. Boddu  
Environmental Processes Branch  
US Army Engineer Research and  
Development Center  
Champaign, IL  
USA

and

Plant Polymer Research Unit, National  
Center for Agricultural Utilization  
Research  
Agricultural Research Service, US  
Department of Agriculture  
Peoria, IL  
USA

ISBN 978-94-024-1199-7                      ISBN 978-94-024-1201-7 (eBook)  
<https://doi.org/10.1007/978-94-024-1201-7>

Library of Congress Control Number: 2017951437

© US Government (outside the USA) 2018

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by Springer Nature  
The registered company is Springer Science+Business Media B.V.  
The registered company address is: Van Godewijkstraat 30, 3311 GX Dordrecht, The Netherlands

# Preface

This monograph summarizes science and technology of select new generation high-energy and insensitive explosives. There is an enormous amount of information being generated and published in the open literature on different areas pertaining to civilian and military uses of these materials. The objectives of this monograph are to provide the professionals with comprehensive information on synthesis, physicochemical, and detonation properties of the explosives. Potential technologies applicable for treatment of contaminated waste streams from manufacturing facilities and environmental matrices are also included. This book provides the reader an insight into the theoretical and empirical models and experimental techniques currently being developed in the field of energetic materials. The material in this book should assist researchers involved in both sensitive and insensitive energetic materials, a program of the United States Department of Defense.

Physicochemical Measurements on Insensitive Munitions Compounds for Environmental Applications—Understanding the environmental impact of energetic materials is critical for their acceptance for use in weapons systems. Predicting their environmental distribution, biotransformation, and determining potential treatment processes assist both decision-makers and scientists in the development process. Combustion of explosives involves complex physicochemical changes and reaction mechanisms. Therefore, there is a need to have knowledge of accurate and good quality data on properties such as solubility, toxicity, enthalpies of formation and combustion, thermal properties, and a host of other properties. We have tried to put together as many properties available in the published literature. Since extensive testing to design high-energy insensitive munitions and formulations are expensive, this monograph should help researchers who use multiphysics modeling programs to achieve high-energy materials and formulations. Thermophysical properties collected in this monograph should be useful in 2-D numerical codes that will simulate slow and fast cook-off, and codes that simulate detonation properties.

This monograph has 11 chapters, and each chapter is devoted to one particular compound with the exception of Chap. 1. Chapter 1 deals with the measurements and estimations of several physical properties important to the characterization,

screening, and utilization of energetic materials. It outlines different experimental methods of measurement of physical properties, and their limitations.

The remaining ten chapters are devoted to a set of new emerging energetic materials. Each chapter considers one energetic compound and enumerates the synthesis methods, structure, physical and chemical properties, decomposition and destruction, detonation characteristics, toxicity, explosive formulations, and detection of that compound. The compounds considered in this monograph are as follows: hexanitrohexaazaisowurtzitane (HNIW, CL-20), 1,1-diamino-2,2-dinitro ethylene (DADE, FOX-7), 2,4-dinitroanisole (DNAN), 5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO), 1,3,3-trinitroazetidine (TNAZ), triacetone triperoxide (TATP), 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 1-azido-2-nitro-2-azapropane (ANAP), N-methyl-4-nitroaniline (MNA), and hexanitrostilbene (HNS). These compounds represent a cross section of sensitive high energetic materials such as TATP and insensitive energetic compounds that are used in different applications.

We have tried to present the current literature on these compounds, and bring together material scattered in different publications. The material presented in this monograph should supplement material found in several other books such as *The Chemistry of Explosives* by J. Akhavan, *Propellants and Explosives* by N. Kubota, *Organic Chemistry of Explosives* by J.P. Agrawal and R. Hodgson, *High Energy Materials* by J.P. Agrawal, *Advanced Processing Technologies for Next-Generation Materials* by T.M. Klapotke, *Liquid Explosives* by J. Liu, and others.

With great appreciation, we take this opportunity to thank the editors at Springer. The authors are thankful to the publishers for agreeing to our repeated requests to postpone submission of the manuscript. Special thanks are extended to Ms. Cynthia Feenstra for her coordination and patience in extending the deadline for submitting the manuscript. We also thank our family members for their support for realization of this book.

Columbia, MO, USA  
Columbia, MO, USA  
Peoria, IL, USA

Dabir S. Viswanath  
Tushar K. Ghosh  
Veera M. Boddu

# Contents

<b>1</b>	<b>Properties of Insensitive Energetic Materials and Their Measurement</b>	<b>1</b>
1.1	Introduction	1
1.2	Experimental Methods	3
1.3	Melting Point	3
1.3.1	Thiele Tube	4
1.3.2	Thomas–Hoover Uni-Melt Device	4
1.3.3	Mel-Temp Apparatus	5
1.4	DSC/DTA Method	6
1.5	Boiling Point	8
1.6	Critical Temperature, Volume, and Temperature	8
1.7	Density	8
1.8	Detonation Velocity	9
1.9	Detonation Pressure	10
1.10	Volatility	13
1.11	Vapor Pressure	13
1.11.1	Knudsen Effusion Method	14
1.11.2	Thermogravimetry Method for Vapor Pressure Determination	15
1.11.3	Comparative Method	18
1.11.4	Vapor Pressure by Gas Chromatography Head Space Method	19
1.12	Strength, Performance, and Brisance of Explosives	20
1.12.1	Strength Tests	21
1.12.2	Performance Tests	24
1.12.3	Brisance	26
1.13	Critical Diameter	31
1.14	Chemical Decomposition	32
1.15	Deflagration	32

1.16	Detonation . . . . .	32
1.17	Sensitivity . . . . .	32
1.17.1	Shock Wave Tests . . . . .	33
1.17.2	Mechanical Impulses . . . . .	33
1.17.3	Friction Sensitivity . . . . .	34
1.17.4	ABL Tests . . . . .	36
1.17.5	BAM Friction Test . . . . .	36
1.18	Electrostatic Discharge (ESD) Test . . . . .	38
1.18.1	Gap Tests-Shock Wave . . . . .	38
1.18.2	Thermal Sensitivity Test . . . . .	39
1.19	Stability . . . . .	40
	References . . . . .	41
<b>2</b>	<b>Hexanitrohexaazaisowurtzitane (HNIW, CL-20)</b> . . . . .	<b>59</b>
2.1	Introduction . . . . .	59
2.2	Synthesis . . . . .	60
2.2.1	Characterization of Polymorphs of CL-20 . . . . .	64
2.2.2	Diffraction Studies . . . . .	67
2.3	Detection . . . . .	69
2.4	Physical and Thermal Properties . . . . .	70
2.4.1	Vapor Pressure . . . . .	72
2.4.2	Heat Capacity and Entropy Data . . . . .	73
2.5	Solubility . . . . .	73
2.6	Decomposition and Destruction . . . . .	74
2.7	Hydrolysis of Hexanitrohexaazaisowurtzitane . . . . .	76
2.8	Biodegradation . . . . .	77
2.9	Spectroscopy . . . . .	81
2.10	Formulations and Detonation Characteristics . . . . .	82
2.11	CL-20 Based Formulations . . . . .	85
2.12	Toxicity . . . . .	88
2.13	Conclusion . . . . .	88
	References . . . . .	88
<b>3</b>	<b>FOX-7 (1,1-Diamino-2,2-Dinitroethylene)</b> . . . . .	<b>101</b>
3.1	Introduction . . . . .	101
3.2	Synthesis . . . . .	102
3.3	Crystallization/Recrystallization . . . . .	108
3.4	Structure . . . . .	112
3.4.1	Polymorphic Forms . . . . .	112
3.4.2	Crystal Structure . . . . .	113
3.5	Thermophysical Data . . . . .	115
3.5.1	Solubility of FOX-7 . . . . .	120
3.6	Detection . . . . .	121
3.7	Decomposition and Destruction . . . . .	123

3.8	Spectroscopy . . . . .	124
3.9	Detonation Properties . . . . .	128
3.10	Cylinder Test . . . . .	130
3.11	FOX-7 Formulation . . . . .	134
3.12	Conclusion . . . . .	135
	References. . . . .	135
<b>4</b>	<b>2,4 Dinitroanisole (DNAN)</b> . . . . .	<b>141</b>
4.1	Introduction . . . . .	141
4.2	Synthesis . . . . .	142
4.3	Structure . . . . .	145
4.3.1	Spectral Data . . . . .	146
4.4	Physical and Chemical Properties . . . . .	147
4.4.1	Solubility in Various Media . . . . .	147
4.4.2	Vapor Pressure . . . . .	151
4.5	Detonation Characteristics. . . . .	152
4.6	Decomposition . . . . .	152
4.7	Biodegradation/Biotransformations . . . . .	152
4.8	Detection . . . . .	153
4.9	Formulation Using DNAN . . . . .	155
	References. . . . .	156
<b>5</b>	<b>5-Nitro-2,4-Dihydro-3H-1,2,4-Triazole-3-One (NTO)</b> . . . . .	<b>163</b>
5.1	Introduction . . . . .	163
5.2	Synthesis . . . . .	163
5.3	Structure . . . . .	167
5.4	Properties . . . . .	168
5.4.1	Heat Capacity and Entropy . . . . .	168
5.4.2	Solubility. . . . .	170
5.4.3	Vapor Pressure of NTO. . . . .	174
5.5	Decomposition and Destruction . . . . .	175
5.5.1	Laser Induced Decomposition . . . . .	178
5.6	Nitration Kinetics . . . . .	179
5.7	Decomposition Kinetic Rates . . . . .	179
5.8	Photocatalytic Degradation . . . . .	180
5.9	Biodegradation of NTO . . . . .	181
5.10	Spectroscopic Analysis of NTO . . . . .	182
5.11	Detonation Characteristics. . . . .	183
5.11.1	Vacuum Stability Test. . . . .	183
5.11.2	Impact Sensitiveness . . . . .	184
5.11.3	Friction Sensitivity Tests . . . . .	185
5.11.4	Electrostatic Discharge Sensitivity. . . . .	185
5.11.5	Thermal Sensitivity . . . . .	185
5.11.6	Shock Sensitivity. . . . .	186



5.12	Detonation Velocity	186
5.13	Detonation Pressure	187
5.14	Formulations	187
5.15	Toxicity	194
5.16	Detection	194
5.17	Conclusion	197
	References	197
<b>6</b>	<b>Hexanitrostilbene (HNS)</b>	<b>213</b>
6.1	Introduction	213
6.2	Synthesis	214
6.2.1	UK Laboratory HNS Process	216
6.2.2	Kompolthy Process	216
6.3	Structure	220
6.4	Polymorphism	223
6.5	Spectra	226
6.6	Sensitivity	226
	References	226
<b>7</b>	<b>N-Methy-4-Nitroaniline (MNA)</b>	<b>233</b>
7.1	Introduction	233
7.2	Solvents	233
7.3	Physical Properties	234
7.4	Solubility	234
7.5	Spectrum	234
	References	238
<b>8</b>	<b>1-Azido-2-Nitro-2-Azapropene (ANAP)</b>	<b>243</b>
8.1	Introduction	243
8.2	Synthesis	243
	References	245
<b>9</b>	<b>1, 3, 5-Triamino-2, 4, 6-Trinitrobenzene (TATB)</b>	<b>247</b>
9.1	Introduction	247
9.2	Synthesis and Manufacture	248
9.3	Structure	251
9.4	Crystal Properties	252
9.5	Physical and Thermodynamic Properties	254
9.6	Thermodynamic Properties	254
9.7	Solubility	256
9.8	Performance	257
9.9	TATB Formulations	258
9.10	Conclusions	259
	References	259

<b>10 Triacetone Triperoxide (TATP)</b> .....	273
10.1 Introduction .....	273
10.2 Synthesis .....	275
10.3 Structure .....	276
10.4 Detection .....	276
10.5 Properties of TATP .....	279
10.6 TATP Decomposition .....	280
10.7 Formulations and Detonation Characteristics .....	280
10.8 Destruction .....	284
References .....	284
<b>11 1,3,3-Trinitroazetidine (TNAZ)</b> .....	293
11.1 Introduction .....	293
11.2 Synthesis .....	293
11.3 Phase Diagrams .....	294
11.4 Thermodynamic Properties .....	295
11.5 Thermal Decomposition/Dissociation .....	298
References .....	299
<b>Appendix 1: Unit</b> .....	309
<b>Appendix 2: Munitions and Dual-Use Items</b> .....	329
<b>Appendix 3: Chemical Weapons Convention (CWC)</b> .....	337
<b>Appendix 4: Chemical Weapons Convention Bulletin</b> .....	349
<b>Appendix 5: CAS RN Reportable Chemicals</b> .....	359
<b>Appendix 6: Material Safety Data</b> .....	401