Potential Replacements of RDX with Low Sensitivities

Thomas M. Klapötke and Jörg Stierstorfer

Energetic Materials Research
University of Munich (LMU)
Butenandtstr. 5-13
Munich, Germany 81377

Introduction

In the field of main charge *explosives*, especially in military applications, many new energetic molecules have been synthesized (*Figure 1*). Based on computational simulations, as well as experiences from the field of organic chemistry, high density *explosive* target molecules (so called high energy density materials: HEDMs) have been defined and can be achieved if the molecular structure contains fused ring and/or strained ring systems.

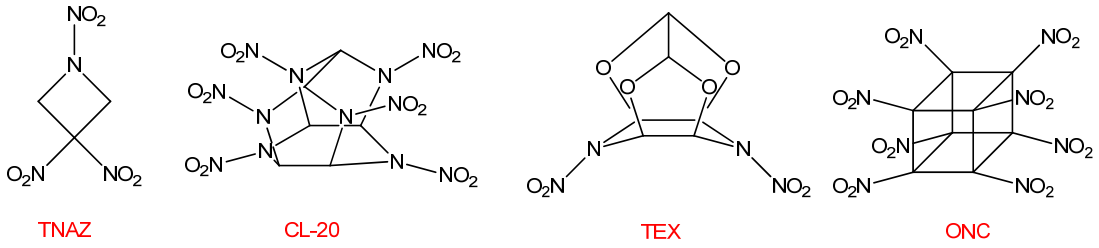

Figure 1. Modern HEDMs

Target molecules, like nitrated cubanes, are predicted to be shock-insensitive and very dense (1.9 − 2.2 g cm^{-3})[1] with great potential as an explosive and a propellant. Although octanitrocubane has been synthesized recently, cubane chemistry is too complicated to produce quantities for use in corresponding charges.[2] Another interesting cage structure, which can be synthesized quite easily, is based on the isowurtzitanes. The two most important molecules representing this class are the 2,4,6,8,10,12-(hexanitro-hexaaza)-tetraazaycloododecane (HINW, CL-20)[3] and 4,10-dinitro-2,4,8,12-tetraoxa-4,10-diaza-tetracycloododecane (TEX).[4] CL-20, in its ε-crystal polymorph, has a density of 2.04 g cm^{-3}, a decomposition temperature of 228 °C.

Highly nitrated small ring heterocycles and carbocycles are interesting as energetic materials too, because of the increased performance expected from the additional energy release (manifested in a higher heat of formation) upon opening of the strained ring system during decomposition. The most widely studied energetic small-ring compound to date is 1,3,3-trinitroazetidine (TNAZ), a potentially melt-castable explosive that has been investigated as a possible replacement for TNT. TNAZ has a melting point of 103–104 °C, a crystal density of 1.84 g cm^{-3} and thermal stability of >240 °C. TNAZ was first synthesized by Archibald et al..[5]

A different area of interest, which has been in focus for the last two decades, is the so called insensitive, less powerful high explosive molecules. The field of the chemical base structures of these materials is very manifold, and therefore only a few prominent examples are given (*Figure 2*). The most traditional insensitive high explosive, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), has an aromatic base structure and is currently the standard for heat resistant, insensitive explosives.[6] Newer ones are related to the work of Pagoria et al. and Ritter et al., and are illustrated by two examples of dinitro-substituted pyridine and pyrazine heterocycles. Pagoria et al. synthesized 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105)[7] which has a density of 1.918 g cm^{-3} and a decomposition point of 354 °C. Ritter and

Lichter reported the synthesis of 2,6-diamino-3,5-dinitropyridine-1-oxide (ANPyO) with a density of 1.878 g cm^{-3} and an mp of >340 °C (dec.).[8] 3-Nitro-1,2,4-triazole-5-one (NTO), easily synthesized in two steps,[9] is used in many new high explosive applications, especially in combination with RDX, designed to be less sensitive.[10] One of the most promising new insensitive explosive is the recently reported 1,1-diamino-2,2-dinitroethylene (FOX-7) with a density of 1.885 g cm^{-3}.

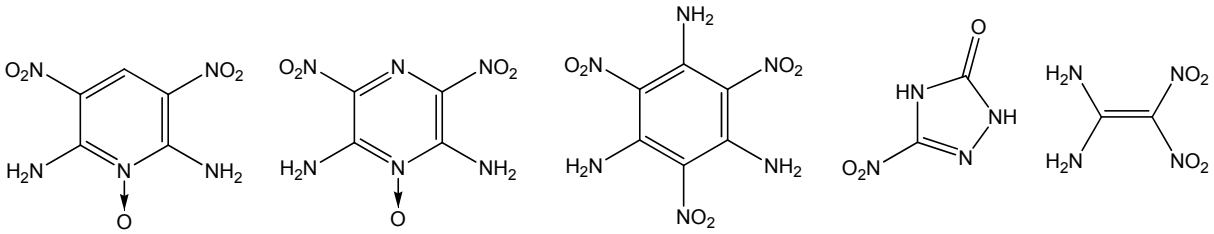

Figure 2. Low sensitive HEDMs

Results and Discussion

In our continuous search of new insensitive energetic materials with high nitrogen and oxygen content for application as secondary explosives, several new or weakly described compounds were synthesized and investigated as replacements for RDX. The syntheses mostly were optimized with regard to their yield, purity and scale. All compounds were fully characterized, including X-ray structures, NMR, IR, and Raman spectroscopy as well as elemental analysis. In addition, the sensitivities towards impact, friction and electrostatic discharge were elucidated using standard BAM methods. The detonation parameters (e.g. detonation energy, detonation pressure, detonation velocity) were calculated using the EXPLO5 computer code, which applies on the solid state densities and calculated (CBS-4M) energies of formations. In strong collaboration with the ARL in Aberdeen proving ground, the thermal stabilities, long-term stabilities and compatibilities of the materials as well as incorporated in explosive mixtures were investigated.

In the following, different molecules are presented, which were investigated to replace hexogen. All performance parameters were calculated with the EXPLO5.03 computer code. The code is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker-Kistiakowsky-Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan-Fickett's equation of state for solid carbon. The calculation of the equilibrium composition of the detonation products is done by applying the modified White, Johnson and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. In comparison to Cheetah, the EXPLO5 code usually underestimates the detonation parameters such as detonation velocity or pressure. The impact and friction sensitivities were determined by BAM methods (1of 6). The temperatures of decompositiuon are given as DSC onset temperatures (heating rate 5° min^{-1}). The densities were mostly determined by low-temperature single crystal X-ray diffraction, in two cases by gas-pycnometry.

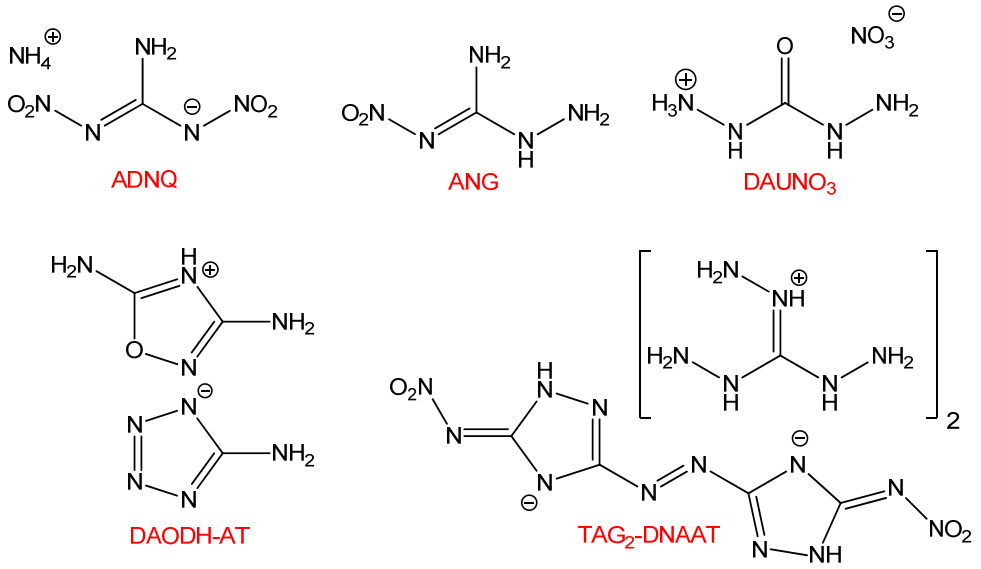

Figure 3. Presented low sensitive HEDMs: Ammonium dinitroguanidine (ADNQ), Amino-nitro-guanidine (ANG), Diaminouronium nitrate ($DAUNO_3$), Triaminoguanidinium dinitriminoazatriazolate (TAG_2-DNAAT) and Diamino-oxadiazolium 5-aminotetrazolate (DAODH-AT).

Table 1 Energetic Properties and calculated detonation parameters.

	RDX	**ADNQ**	**ANG**	**$DAUNO_3$**	**DAODH-AT**	**TAG_2-DNAAT**
Formula	$C_3H_6N_6O_6$	$CH_6N_6O_4$	$CH_5N_5O_2$	$CH_7N_5O_4$	$C_3H_7N_9O$	$C_6H_{20}N_{24}O_4$
FW [a] / g mol^{-1}	222.12	166.09	119.08	153.10	185.15	492.38
IS [b] / J	7	10	20	9	>40	>40
FS [c] / N	120	252	144	288	>360	>360
ESD [d] / J	0.1 - 0.2	0.4	0.15	0.6	1.0	1.0
N [e] / %	37.8	50.60	58.81	45.74	68.09	69.27
Ω [f] / %	–21.6	-9.63	-33.6	-15.67	-73.45	58.49
$T_{Dec.}$ [g] / °C	210	197	184	242	170	212
ρ [h] / g cm^{-3}	1.80	1.735	1.767	1.782	1.76*	1.70*
$\Delta_f H_m°$ [i] / kJ mol^{-1}	70	-1.5	77	-180	680	260
$\Delta_f U°$ [j] / kJ kg^{-1}	417	81.0	770	-1048	4034	2332
EXPLO5 values:						
$-\Delta_{Ex}U°$ [k] / kJ kg^{-1}	6038	5193	4934	5014	4034	4681
T_{det} [l] / K	4368	3828	3436	3480	3719	3213
P_{CJ} [m] / kbar	341	327	323	317	348	300
$V_{Det.}$ [n] / m s^{-1}	8906	9066	8977	8829	9382	8890
V_o [q] / L kg^{-1}	793	934	890	925	802	352

[a] formula weight; [b] impact sensitivity (BAM drophammer, method: 1 of 6); [c] impact sensitivity (BAM friction tester, method: 1 of 6); [d] electrical spark sensitivity (OZM small scale electrical discharge device); [e] nitrogen content; [f] oxygen balance; [g] temperature of decomposition; [h] X-ray density; [i] heat of formation; [j] energy of formation; [k] energy of explosion; [l] explosion temperature; [m] detonation pressure (Chapman-Jouguet); [n] detonation velocity; [q] volume of explosion gases; * determined by gas-pycnometry.

Acknowledgments

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the U.S. Army Research Laboratory (ARL), the Armament Research, Development and Engineering Center (ARDEC), the Strategic Environmental Research and Development Program (SERDP) and the Office of Naval Research (ONR Global, title: “Synthesis and Characterization of New High Energy Dense Oxidizers (HEDO) - NICOP Effort ”) under contract nos. W911NF-09-2-0018 (ARL), W911NF-09-1-0120 (ARDEC), W011NF-09-1-0056 (ARDEC) and 10 WPSEED01-002 / WP-1765 (SERDP) is gratefully acknowledged. The authors acknowledge collaborations with Dr. Mila Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. Muhamed Sucesca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice and Brad Forch (ARL, Aberdeen, Proving Ground, MD) and Mr. Gary Chen (ARDEC, Picatinny Arsenal, NJ) for many helpful and inspired discussions and support of our work. The authors thank Franz Martin, Niko Fischer, Alexander Penger, Thomas Altenburg and Norbert Mayr for their excellent synthetic work.

References

[1] a) A. I. Kitaigorodsky *Molecular Crystals and Molecules*, Academic Press, New York, **1973**; b) A. Immirzi, B. Perini, *Acta Cryst.* **1977**, *33(A)*, 216; c) H. H. Cady, *Estimation of the Density of Organic Explosives from Their Structural Formulas*, Report #LA-7760-MS, Los Alamos National Laboratory, Los Alamos, NM, **1979**; d) D. A. Cichra, J. R. Holden, C. Dickinson, *Estimation of “Normal” Densities of Organic Explosives from Empirical Atomic Volumes*, Report #NSWC-TR-79-273, Naval Surface Warfare Center (White Oak), Silver Spring, MD, **1980**; e) J. R. Stine, *Prediction of Crystal Densities of Organic Explosives by Group Additivity*, Report #LA-8920, Los Alamos National Laboratory, Los Alamos, NM, **1981**; f) J. Alster, S. Iyer, O. Sandus O. in Chemistry and Physics of Energetic Materials (Bulusu S. N. (ed.)), Kluwer, Dordrecht, **1990**, chap. 28; g) J. R. Holden, Z. Du, H. L. Ammon, *J. Comput. Chem.* **1993**, *13*, 422; h) K. Jayasuriya, *Computational Investigation of New Potential Explosive and Propellant Molecules*, 14th Annual Working Group Institute on HEDMs, Kiamesha Lake, NY, **1995**, 2943; i) J. S. Murray, T. Brinck, P. Politzer, *Chem. Phys.* **1996**, *204*, 289.

[2] a) M.-A.Zhang, P. E. Eaton, R. Gilardi, *Angew. Chem. Int. Ed.* **2000**, *39(2)*, 401; b) P. E.; *Propellants, Expl. Pyrotech.* **2002**, *27*, 1.

[3] a) G. P. Sollott, J. Alster, E. E. Gilbert, O. Sandus, N. Slagg, *J. Energ. Mater.* **1986**, *4*, 5; b) J. Boileau, L. Emeury, J.-P. Kehren, United States Patent 4,487,938, **1984**; c) Nielsen, A. T. Unites States Patent 5,693,794, **1997**.

[4] J. Hanks, T. Highsmith, A. Sanderson, K. Warner, Worthington, J. *33th Int. Annual Conf. of ICT*, Karlsruhe, Germany, **2002**, P129.

[5] G. Doddi, P. Mencarelli, A. Razzini, F. Stegel, *J. Org. Chem.* **1979**, *44*, 2321.

[6] a) S. F. Rice, R. L. Simpson, Lawrence Livermore National Laboratory, Report UCRL-LR-103683, Livermore, CA, **1990**; b) A. R. Mitchell, P. F. Pagoria; R. D. Schmidt, Unites State Patent 6,069,277, **2000**.

[7] P. F. Pagoria, A. R. Mitchell, R. D. Schmidt, R. L. Simpson, F. Garcia, J. Forbes, J. Cutting, R. Lee, R. Swansiger, D. M. Hoffman, *Presented at the Insensitive Munitions and Energetic Materials Technology Symposium*, San Diego, CA, **1998**.

[8] H. Ritter, H. H. Licht, *J. Heterocycl. Chem* **1995**, *32*, 585.

[9] A. R. Basal, V. L. Zbarsky, V. F. Zhilin, *32th Int. Annual Conf. of ICT*, Karlsruhe, Germany, **2001**, P73.

[10] A. Becuwe, A. Delcos, *Propellants, Explos. Pyrotech.* **1993**, *18*, 1.