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Preface

This book summarizes some recent developments in the area of high-energy high-density (HEDM) materials. Rather than being comprehensive in scope, emphasis is given to structural and bonding features of highly energetic materials with possible applications as high explosives (secondary explosives) or propellants. In this book we do not focus on primary explosives (e.g. lead azide replacements) since by definition the explosive performance (detonation velocity and detonation pressure) of such materials – although very sensitive – are much less energetic than secondary (high) explosives.

Modern HEDMs derive most of their energy (i) from oxidation of the carbon backbone, as in traditional energetic materials, (ii) from ring or cage strain, or (iii) from their very high positive heat of formation. Examples of the first class are traditional explosives, such as TNT, RDX and HMX. Modern nitro-compounds, such as CL-20 or the recently reported hepta- and octanitrocubanes, belong to the second group of explosives and possess very high densities and enhance the energies utilizing substantial cage strain. Members of the third class of compounds are high-nitrogen compounds (up to 85% nitrogen content), such as aminotetrazole and nitrotetrazole derivatives, which show the desired remarkable insensitivity to electrostatic discharge, friction and impact, while having very high positive heats of formation and therefore very high explosive powers.

The synthesis of energetic, non-nuclear materials for military application has been a long-term goal in various academic and military research groups worldwide. Some of the current challenges that face HEDM scientists are:

- Demand for environmentally compatible and toxicologically acceptable explosives and propellants. Examples are replacements for TNT, RDX and HMX since nitro-explosives per se, as well as their environmental transformation products, are toxic.
- Demand of all the services for more destructive energy delivered to the target.
- Minimization of unwanted effects: low collateral damage munitions, i.e. munitions that cause little damage aside from damage to the intended target, have become more important as sites of military interest are increasingly co-located with civilian population centers.

- Continuing interest in insensitivity: insensitive munitions for reduced vulnerability of munitions stores and increased survivability of munitions that are subjected to very stressful conditions under their normal usage.
- Continuing interest in low observable plumes (no signature of a missile, smokeless combustion) and erosion-reduced gun propellants.

The six chapters in this book all focus on various aspects of the structure and bonding of modern HEDMs. While the first four chapters (Bellamy, Shreeve, Klapötke, Chapman) discuss synthetic aspects of energetic materials, chapter five (Rice) gives emphasis to computational aspects of nitrogen-rich HEDMs, while the last chapter (Zeman) is devoted to the sensitivities of high energy compounds. In the synthetic part of this book, the first chapter (Bellamy) describes the most recent aspects of the chemistry of Fox-7, a remarkably insensitive high-nitro explosive. The following two chapters concentrate on modern high-nitrogen compounds: nitrogen-rich heterocycles (Shreeve) and new nitrogen-rich high explosives (Klapötke). The last preparative chapter (Chapman) summarizes the work on the synthesis and structures of cyclic nitramines, new (difluoramino)alkanes and non-nitramines. In the theoretical chapter (Rice), emphasis is given to a variety of computational procedures to predict the properties of energetic nitrogen-rich HEDMs. Finally, the last chapter (Zeman) presents a survey of studies into the sensitivity of HEDMs, focusing mainly on impact and shock sensitivities.

It is no coincidence that three out of six chapters are directed towards the synthesis and computation of high-nitrogen compounds. Nitrogen is unique amongst all other elements of the periodic table insofar that the bond energy per two-electron bond increases from a single over a double to a triple bond. For carbon the situation is the opposite and one might expect acetylene to polymerize in an exothermic reaction whereas dinitrogen is more stable than any other polynitrogen species. Therefore, high-nitrogen HEDMs with N–N bond orders of less than two may provide some solutions to the above-mentioned challenges: very high explosive energy, low toxicity reaction products (N_2), no observable plumes or signatures and reduced gun erosion. It is still too early in the development of such materials to assess whether they will live up to their potential, but they nonetheless represent a very exciting and challenging new area of chemistry.

Thomas M. Klapötke

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