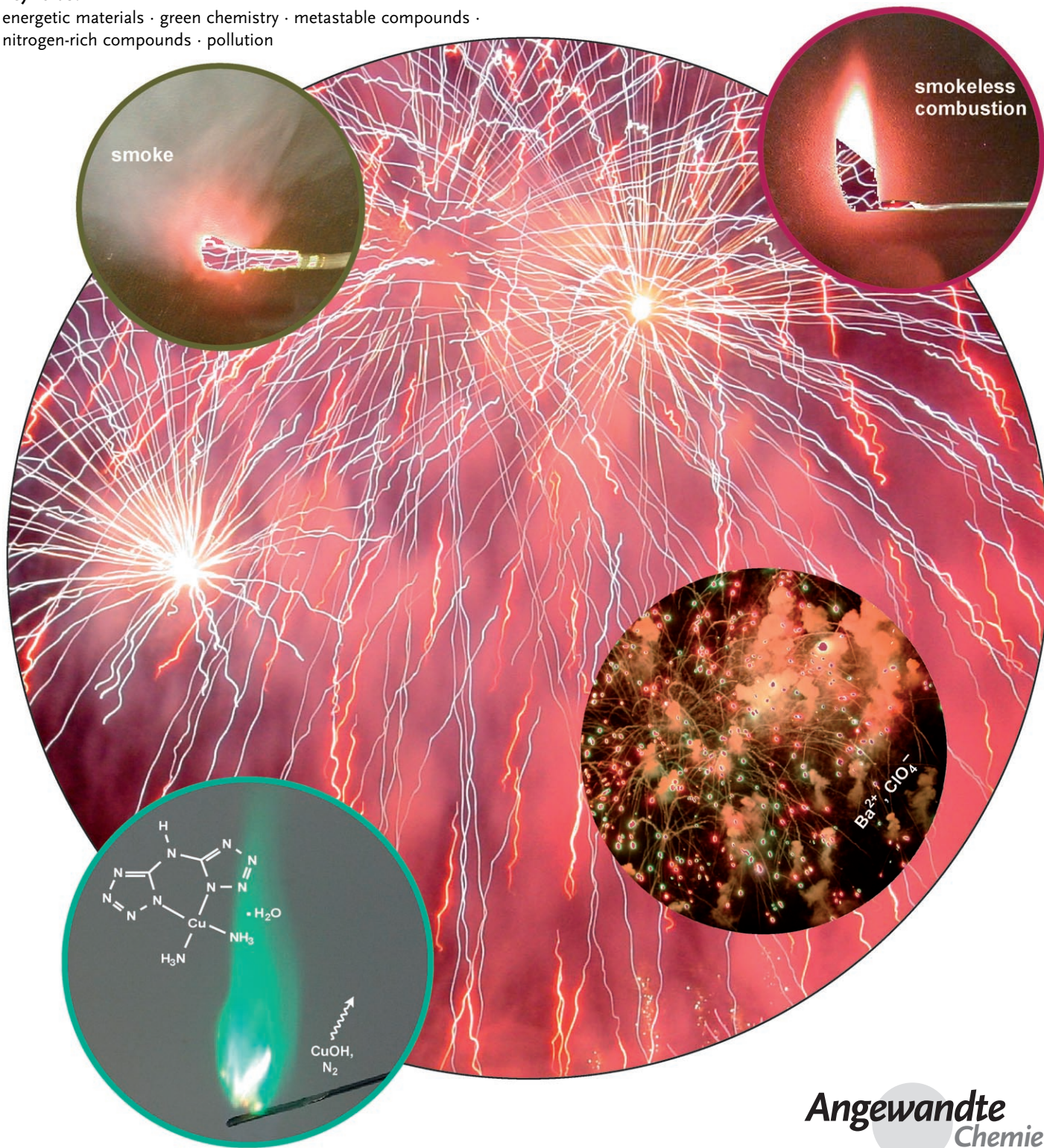


Pyrotechnics

“Green” Pyrotechnics: A Chemists’ Challenge*Georg Steinhauser and Thomas M. Klapötke****Keywords:**energetic materials · green chemistry · metastable compounds ·
nitrogen-rich compounds · pollution**Angewandte**
Chemie

Fireworks are probably the application of chemistry which resonates best with the general public. However, fireworks and (civil and military) pyrotechnic applications cause environmental pollution and thus have given rise to the development of new, environmentally friendly pyrotechnic compounds and formulations. Nitrogen-rich energetic materials, such as the derivatives of tetrazoles and tetrazines, are about to revolutionize traditional pyrotechnic compositions. This Review summarizes the sources of pollution in current formulations and recent efforts toward “green” pyrotechnics.

From the Contents

1. Introduction	3331
2. Constituents of Pyrotechnics	3331
3. The Pollutant Puzzle	3335
4. Nitrogen-Rich Compounds: The Greening of Pyrotechnics	3337
5. Outlook and Conclusion	3345

1. Introduction

With the discovery that combustion of organic matter is accelerated by saltpeter (potassium nitrate) in China several centuries BC and invention of gunpowder (also known as black powder) in 220 BC, mankind began a fascination with fireworks that will probably never cease. However, today, pyrotechnics offer multifaceted technical applications in addition to fireworks, such as airbags, fire extinguishers, (road) flares, matches, the production of nanoporous foams and propellants. The development and investigation of pyrotechnics is part of the rapidly expanding scientific field of energetic materials.^[1] Today, the combined US explosives and pyrotechnics demand is \$2.6 billion. In Germany, approximately \$80 million are annually spent on around 30 000 tons of fireworks.^[2]

The basic components of any pyrotechnic device are the oxidizer and the reducing agent or fuel. Other (optional) constituents are binders, propellants, coloring agents, and sound or smoke producing agents.^[3] Pyrotechnics are traditionally mixtures of substances, this is in contrast to high explosives which may consist of only one compound combining both of the necessary components in the same molecule. Most pyrotechnic reactions are therefore solid-state reactions. The right particle size and an absolute homogeneity are therefore essential.^[4]

The basic component of any traditional civil firework rocket or shell is still gunpowder (a mixture of 75 % potassium nitrate, 15 % charcoal, and 10 % sulfur). Its composition may vary depending on application (50–85 % KNO₃, 0–30 % charcoal, 0–50 % sulfur).^[5] For military purposes, pyrotechnics are generally made of components other than gunpowder to provide better performance, neglecting higher costs or toxicity. Typical military applications of pyrotechnics include missile propellants, flares, igniters and initiators, delay devices in blasting caps, camouflage and delusion devices, signal fires, tracers, incendiary devices, gas or smoke generators, and aerial countermeasures (decoy devices).^[6]

2. Constituents of Pyrotechnics

2.1. Fuels

The reducing agent (fuel) is chosen depending on the desired pyrotechnic effect, for example, for bright fireworks, metal powders are used, including magnesium (and other alkaline-earth metals), aluminum, titanium, iron, copper, zinc and zirconium. Non-metals, such as charcoal, sulfur, and red phosphorus, metalloids, such as silicon and boron, and a variety of organic materials or natural products, such as flour, are also used as fuels. Magnesium is one of the most common fuels (because it is inexpensive), though it has some undesirable and hazardous properties (especially its reactivity with water). Metal fuels also include alloys, such as Magnalium (Mg–Al 50:50, a solid solution of Al₃Mg₂ in Al₂Mg₃ with a melting point of 460 °C^[7]), Zr alloys, Ni–Fe alloys. More exotic fuels include beryllium, chromium, nickel, and tungsten.

In recent years, the use of nanometer-sized metal-particle fuels has been topic of pyrotechnic research. They are introduced into the pores of nanostructured metal oxides (especially iron oxides), produced in sol–gel processes. This technique allows a larger degree of homogeneity when utilized in a pyrotechnic mixture and provides a better performance and lower sensitivity^[4,8]. Sensitivities are discussed in ref. [9]. A military application of nanomaterials is found in infrared countermeasures, in which pyrotechnic formulations with ultrafine aluminum-based ALEX^[10] are used as combustion enhancers. They show promising features

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as decoy devices by simulating the infrared signature of an aircraft's kerosene plume.^[6c–f]

2.2. Oxidizers

2.2.1. Conventional Oxidizers

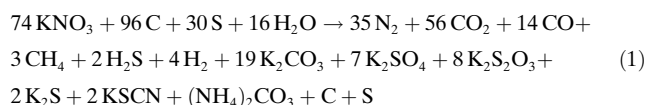
Oxidizers are traditionally nitrates,^[11] perchlorates, and occasionally chlorates of alkali or alkaline-earth metals; ammonium nitrate and ammonium perchlorate are also used. Somewhat less frequently, organic compounds such as guanidinium nitrate or nitroguanidinium nitrate are used. In some cases, nitronium perchlorate, chromates of barium, calcium, or lead, potassium dichromate, and alkaline-earth peroxides (SrO₂, BaO₂), find applications as oxidizers. Occasionally mixtures containing Fe₃O₄ or lead(II) nitrate are used. Nitrates need higher temperatures to decompose and set their oxygen atoms free than, for example, perchlorates. Therefore nitrates are usually used in combination with metal fuels.

Pyrotechnic formulations are thermodynamically metastable. There is thus the inherent risk that in some cases, hazardous mixtures might react beyond the intended frame.^[12] In general, water or hygroscopic compounds are unacceptable in pyrotechnic compositions, because they may inhibit the reaction, or they can lead to unintended hazardous reactions, for example, the oxidation of magnesium metal by Cu^{II} ions, which can lead to self-ignition.

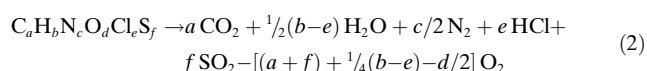
2.2.2. Oxygen Balance

The potential of an oxidizer in a mixture or an oxidizing group in a compound is primarily determined by the oxygen balance (Ω). This value (given as a percentage) represents the (theoretical) ability of a system to perform complete combustion (that is, a complete and residue-free consumption of the fuel): An oxygen balance of 0 indicates a stoichiometric mixture of fuel atoms and oxidizing atoms. A negative oxygen balance (negative Ω values) indicates a system in which unburned fuel is left behind or that requires atmospheric oxygen for complete combustion. A positive oxygen balance indicates a system in which there is an excess of oxygen for the combustion of the fuel atoms. To obtain the exact oxygen balance, a fundamental, experimentally based understanding

of all of the chemical reactions taking place is a prerequisite. In some cases, this can be more complicated than might be thought. For example, the reactions of combustion for gunpowder with the composition of 75.7% potassium nitrate, 11.7% charcoal, 9.7% sulfur, and 2.9% moisture are approximated by Equation (1).^[5]



In a simplified approach, the combustion of the molecule (or mixture) C_aH_bN_cO_dCl_eS_f can be assumed as in Equation (2). The oxygen balance (Ω) of this molecule (with the molecular mass M) is calculated according to Equation (3).^[13]



$$\Omega (\%) = -[(a+f) + \frac{1}{4}(b-e) - d/2] (32/M) 100 \quad (3)$$

The oxygen balance is of great importance for the reaction rate and the heat of the reaction. By varying the oxygen balance, it is possible to significantly influence both factors.^[8]

2.2.3. Alternative Redox-Reactions

Pyrotechnic mixtures are not limited to those using oxygen as the oxidizing species. Alternative redox pairs are based on metals and halogenated organic compounds or polymers, such as magnesium/Teflon/Viton (abbreviated MTV) mixtures.^[14] The redox reaction of the combustion of a MTV mixture is given in Equation (4).



MTV mixtures are often used in aerial countermeasures (decoy flares),^[6f] tracking flares, propellants, signaling applications, and incendiary devices.^[15] Derivatives of these compositions using poly(carbon monofluoride) ((CF)_n), also known as graphite fluoride) and magnesium^[16] or other fuels (such as, boron, titanium, silicon or Si alloys) have also been investigated recently.^[17]



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Another widely used example of alternative redox pairs is the so-called Berger mixture for the generation of dense, gray smoke using zinc, aluminum or zinc oxide, and hexachloroethane.^[18] Its combustion produces smoke in the form of zinc chloride aerosols, especially in high ambient humidity [Eq. (5)].



2.3. Coloring Agents

The visible spectrum can be summarized by characteristic frequency ranges (Table 1). Light emitted within a particular wavelength range can be described as monochromatic.

Table 1: Wavelength ranges of spectral colors.

Color	Wavelength [nm]
infrared	> 700
red	700–610
yellow	610–570
green	570–500
blue	500–450
violet	450–400
ultraviolet	< 400

However, when colored light is generated pyrotechnically, it is not monochromatic, because it also contains spectral components outside the desired spectral range. The reason for this is that the energy of a photon emitted is characteristic to the relaxation of an excited electron. Atoms or molecules, when excited by high temperatures (about 3000 K), usually produce several strong emission lines. Only a few elements have principal emission lines lying within the narrow visible range. An example for such an element is sodium with an emission that appears at about 590 nm. Table 2 shows the emission bands of simple molecules and atoms of interest in pyrotechnics. For colored flares, the colors red, green, and yellow are of particular interest. Some typical flare compositions are summarized in Table 3.

Colors in fireworks are obtained by using metals or metal compounds which, upon thermal excitation, emit at characteristic frequencies in the visible spectra (Figure 1). In general, sodium produces yellow luminescence, strontium red, barium green, and copper green or blue. The primary light-emitting species have been determined to be atomic Na for yellow, SrOH and SrCl for red, and BaCl, BaOH and, to a smaller extent, CuCl for bluish-green effects.^[11,19] In barium containing flares, BaO is also a strong emitter. The hydrogen needed to form the hydroxides (SrOH and BaOH) comes from the decomposition of the binder or polyvinylchloride (PVC; Table 3). There is a controversy about the emitting species of blue light, whether it is Cu_3Cl_3 ^[21] or—more likely—CuCl.^[22] Less frequently, calcium is used to produce red, and potassium for violet light. Both show less-intense luminescence than the other elements or combinations of elements.

From Table 2 it is apparent that, chlorides are largely responsible for the emission of a colored spectrum. This effect

Table 2: Spectra of atoms and simple molecules of interest in pyrotechnics. Values are taken from references [18–20].

Element	Emitting species	λ [nm]	Color
lithium	atomic Li	670.8	red
		460	blue
		413	violet
		497	bluish-green
		427	violet
sodium	atomic Na	589.0, 589.6	yellow
		420–460	violet-blue
		510–550	green
copper	CuCl	661.4, 662.0, 674.5, 675.6	red
		623.9, 636.2, 648.5	orange
		393.7, 396.1, 400.9	violet
		605.0, 646.0	orange
		659.0, 667.5, 682.0	red
strontium	SrCl	460.7	blue
		507, 513.8, 516.2, 524.1, 532.1, 649	green
		487, 512	red
		604, 610, 617, 622, 629	greenish-blue
		553.5, 660	green
barium	atomic Sr	553.5, 660	red

Table 3: Some colored flare compositions by wt%.^[19]

Ingredient	Red Navy	Red Highway	Green Navy	Yellow Navy
Mg	24.4		21.0	30.3
KClO ₄	20.5	6.0	32.5	21.0
Sr(NO ₃) ₂	34.7	74.0		
Ba(NO ₃) ₂			22.5	20.0
PVC	11.4		12.0	
Na ₂ C ₂ O ₄				19.8
Cu powder			7.0	
Asphaltum	9.0			3.9
Binder		10.0	5.0	5.0
S ₈		10.0		



Figure 1. Colors in fireworks.

is due to the increased volatility of chlorides. There is a lot of truth on the old pyrotechnic saying “chlorides color”. Also, chlorine donors in magnesium-fueled compositions give rise

to improved color quality as a result of the formation of MgCl molecules, which help by reducing the incandescent emission (similar to “blackbody” radiation) of the MgO particles.^[7,18] Both are grounds for the addition of inorganic chlorides (such as CuCl) or, more often, C₂Cl₆, PVC powder (see Table 3), or other organic chlorides (up to 10% of the pyrotechnic formulation) as a chlorine source.

As stated above, it is important to avoid hygroscopic compounds in the pyrotechnic mixture. Therefore coloring agents, such as NaCl, NaNO₃, or SrCl₂, are less-frequently used than the sodium or strontium oxalates or cryolite (Na₃AlF₆). These substances decompose at high temperature and form chlorides with the chloride donor or they are atomized.

Apart from strontium, a somewhat more exotic (and less effective) coloring agent for red flame colors is lithium.^[23] It can be applied as an oxidizer (as perchlorate, nitrate, dinitramide, chlorate, nitroformate etc.) or as a fuel (in particular, metallic lithium, several hydrides, and lithium boride are discussed in literature).^[20a] Lithium stands out against other elements because of its low specific weight. This makes applications of metallic lithium for MTV-like pyrotechnics interesting for infrared (aerial) decoys and lithium hydride as a gas generator in acoustic (naval) decoys.^[20a]

In special cases, elements such as rubidium and cesium, find application in technical or military pyrotechnics. Both elements produce bluish-violet flame colors in the Bunsen burner flame, however, of most interest are their emissions in the far red (rubidium) and near infrared (cesium).^[24]

Based on the results of a laboratory study, the application of rare-earth elements as possible flame-coloring agents has been suggested. However, no practical examples are known.^[25] Some of the emission bands of the atomic rare-earth elements or, more likely, their monoxides, might find application as coloring agents in pyrotechnics. The monoxides show some analogy to the monochlorides of calcium, strontium, or barium. In both types, one free electron is readily excited by molecular collision and thus provides the flame color. In particular yttrium (deep red) and ytterbium (grass green) show promising flame colors, not only when injected into a inductively coupled plasma (ICP) flame, but also in an acetylene/air flame (2550 K). Some of the rare-earth metals (e.g. Y, Er, Tm, Lu) or corrosion-resistant alloys thereof might be applied as raw materials for colored sparks in fireworks.

Some boric acid esters burn with a green flame, which suggests a possible application of boron compounds in pyrotechnics. Although, their color intensity cannot compete with barium-based formulations, some pyrotechnic compositions with boric acid as the coloring agent have been tested and show a green flame color with good color purity.^[26] It has been reported that boron, as a fuel, combusts in oxygen to form B₂O₃, BO₂, and BO in the gas phase.^[27] The main emitting species in this case is boron dioxide BO₂.^[25] In another study, the infrared emission of boron/alkali-metal nitrate formulations has been investigated. The principal products found were alkali-metal metaborates, B₂O_{3(g)}, BO_(g), and B₂O_{2(g)}.^[28]

2.4. Binders

Binders are important constituents of pyrotechnics, and will usually constitute several weight percent of the pyrotechnic charge. They provide mechanical stability, and by sealing the components to some extent they increase the water resistance of pyrotechnic devices. Their main role though is preventing the segregation of mixtures into their components during manufacture, transport, and storage. However, two main short-comings of binders are well-known and explain recent efforts to develop improved binders: Non-energetic binders can either be water-soluble (such as, dextrin, polyvinyl alcohol, or Arabic rubber) or organic-solvents-based (such as, vinyl alcohol acetate resin, polymethyl methacrylate,^[29] or other organic polymers), or solvent-free materials, such as some epoxy binders or Laminac^[30] (an unsaturated polyester with styrene crosslinks), which binds upon addition of a catalyst. Non-energetic binders act as retardants and decrease reaction rates.^[8] In some cases, this may be the desired effect, but usually it is not. Interestingly, the heat of reaction is only marginally influenced by the content of binders (typically a few per cent).

In contrast to the retarding effect of inert non-energetic organic binders, energetic binders such as glycidyl azide polymer (GAP), polynitropolyphenylene, or nitrocellulose (solvent: acetone) contribute energy to the reaction. Unfortunately, such energetic binders usually contain reactive functional groups (primarily azido, nitrate, nitro, and hydroxy groups), which can lead to undesired reactions with the energetic material.^[31]

In our group, we focus on the synthesis of tetrazole-containing polymers as alternatives to conventional binders.^[32] Another alternative that has been suggested is the application of silicones.^[33]

2.5. Propellants

Propellants are designed to produce high temperatures and pressure in a closed chamber to accelerate projectiles, rockets, or missiles by means of the resulting propulsive force. In general, rapid but defined burning rates and high temperatures are prerequisites for a propellant. Depending on their composition, there are two major groups of solid propellants: homogeneous (single-, double-, and triple-base propellants) and heterogeneous propellants (composite and granulated propellants).^[13,34]

Single-base propellants use nitrocellulose (NC), or more precisely, the nitrates of cellulose, as the main constituent (NC content 85–96%). Other constituents are chemical stabilizers such as, diphenyl amine^[13] and inert or energetic plasticizers, such as, dibutyl phthalate, dibutyl sebacate, camphor, or the isomeric mixture of 2,4-dinitrotoluene and 2,6-dinitrotoluene, respectively.^[34a] In addition to the improvement of the mechanical properties of the propellant, inert plasticizers as well as flame suppressors (such as, potassium sulfate or nitrate) act as retardants and coolants, whereas energetic plasticizers contribute somewhat to the total energy output. Single-base propellants are used for all

kinds of ammunition for small arms as well as cannons, howitzers, tank, aircraft, and anti-aircraft weaponry. The shape and particle size of the propellant mixture is essential for its designated application.

Double-base (“smokeless”) propellants were developed for long distance shooting with large caliber cannons needing higher bullet speeds and thus more energetic propellants.^[34a] Therefore these propellants use nitrocellulose and nitroglycerine (NG) or other liquid nitrate esters. Because of problems arising from the high freezing point of pure NG (13°C),^[35] modern mixtures of NG with the nitrates of glycoles such as diethylene glycol, trimethylene glycol, or other alcohols are used, or the NG is replaced completely. Smokeless double-base propellants consist to 50–60% NC and 30–49% NG or the alternative nitrates listed above.^[34a]

Triple-base propellants contain nitroguanidine (NQ) as a third constituent in addition to nitrocellulose and nitroglycerine. Nitroguanidine has a low flame temperature but a high nitrogen content. Thus, a large volume of gas is produced upon ignition of such “cold powders”. There use prevents damage to the barrel of large-caliber weaponry.^[34b]

Long distance solid-rockets and missiles use heterogeneous propellants. These composite propellants consist of an oxidizer, such as, ammonium perchlorate (AP) (or ammonium nitrate) and a fuel, such as, aluminum. The ignition of such a rocket motor produces a huge cloud of smoke particles and hydrochloric acid.

In general, the aim is to produce a large amount of (gaseous) combustion products with a low molecular mass (M_c) and high combustion temperatures (T_c), so as to maximize the specific impulse (I_{sp})^[5,13] [Eq. (6)].

$$I_{sp} \approx (T_c/M_c)^{1/2} \quad (6)$$

Therefore, beryllium with its low atomic weight is occasionally used as a fuel for propellants in military applications.^[5] For the same reason, carbon monoxide is a desired reaction product, especially in carbon-fueled military propellants, it is a lighter molecule than carbon dioxide and thus provides higher specific impulse and thrust. Military propellant mixtures are therefore often characterized by a negative oxygen balance.

Gunpowder is a heterogeneous or composite propellant and a typical representative of the sub-group of granulated propellants—a propellant in a loosely packed shape.^[13] The mechanical properties of the propellant grains are very important because the propellant’s burning rate is a function of the linear burning rate and the propellant’s specific surface. If the pressure of the burning propellant causes damage to the grains, this will enlarge the specific surface and thus increase the pressure in the combustion chamber.

In civil fireworks, gunpowder is still used as the main propellant for rockets and shells. Other propellants use an oxidizer and charcoal or organic fuel.^[18] The high carbon content of this fuel causes smoke upon combustion. Moreover, corrosion caused by the acidic residues generated by the combustion of gunpowder and a large muzzle flash are profound disadvantages of this propellant for use in military applications.

In contrast to solid propellants, which are placed directly in the combustion chamber, liquid propellants are injected from external tank into the chamber at the time of ignition. There are two classes of liquid propellants: monopropellants (liquid propellants consisting of a single substance or a homogeneous mixture of substances, such as 80–99% hydrogen peroxide and hydrazine) and bipropellants: A fuel and an oxidizer are injected simultaneously, examples of such fuels are hydrocarbons, alcohols, amines, or hydrazines, as oxidizers hydrogen peroxide, concentrated nitric acid, or nitrogen dioxide are used.^[34b] The two components are stored in separate tanks and their simultaneous injection into the combustion chamber initiates the reaction.

3. The Pollutant Puzzle

Fireworks, though spectacular and entertaining, are a source of concern because of environmental pollution (beyond noise). Several toxic substances are released upon explosion, deflagration or burning of the pyrotechnics and which are harmful to the environment. This problem was initially identified decades ago^[36], however efforts to develop environmentally friendly products are recent. as can be seen from the growing number of scientific articles in recent years in this field (focusing on environmental analyses as well as on syntheses of new energetic compounds).^[1,37]

The development of “green” pyrotechnics is under considerable cost pressure, since it is difficult for new products to compete with the low cost of traditional formulations. Green pyrotechnics therefore need governmental or other external support to succeed. Perhaps this Review can help to catalyze this process by providing a fact-oriented overview of the challenges in this field and their potential solutions.

Several poisonous substances are known to be released in the course of a pyrotechnic application. A firework up in the sky disperses the pollutants over a large area. In other cases, such as handheld military flares, however, inhalation of toxic combustion products exhibits a severe health threat. The most important hazards are summarized and discussed below.

3.1. Heavy Metals

Fireworks are closely associated to the emission of heavy-metal aerosols.^[38] The green luminescence effects in pyrotechnic devices are usually generated by volatile barium compounds. In fireworks, for example, barium nitrate is used as both oxidant and coloring agent.

Water-soluble Ba^{II} compounds, such as $BaCl_2$, BaO , and $Ba(OH)_2$, are very poisonous and are all possible products of pyrotechnic activity. Their inhalation has cardiotoxic and bronchoconstrictor effects.^[39] Kulshrestra et al.^[40] found the barium concentrations in air increased by more than a factor of 1000 in the course of the Indian Diwali festival (the festival of lights, traditionally accompanied by fireworks and fire-crackers) compared to the usual background. Thus, in terms of green chemistry, the barium nitrate content makes the green-luminescent pyrotechnics the “dirtiest bombs” of all.

In propellants, compounds such as lead(II) salicylate, stearate or, 2-ethylhexanonate are utilized as burn rate catalysts.^[13] In other cases, lead oxides, such as PbO, PbO₂, and Pb₃O₄^[41] or lead(II) chromate or nitrate^[42] are, or have been used, as oxidizers in pyrotechnics, especially in “electric matches” (non-explosive fuses). They are utilized for all kinds of pyrotechnic and technical initiation purposes. Furthermore, these lead oxides are occasionally constituents of crackling fireworks and millisecond-delay blasting caps.^[43] Recently, efforts at making lead-free electric matches have increased, through the utilization of nanoscale thermite materials, so-called metastable intermolecular composites (MIC).^[44] Apart from avoiding lead compounds, these MIC are characterized by a decreased sensitivity to friction, impact, and heat, coupled with good performance (high combustion temperature). A few years ago, the contribution of fireworks to the total annual emission and deposition of lead was estimated to be at most 0.8%.^[41a]

Workers in a pyrotechnics factory are exposed to dust of the heavy metal compounds and other poisons every day. In some cases, this chronic exposure can lead to diseases of lungs, eyes, skin, and kidneys. A burning issue in this respect is child labor.^[37b] Chromium was found in scalp hair of Indian factory workers and was identified as the cause of headaches and dizziness.^[45] The toxicity of chromium is very much dependent on the oxidation state of the ion, Cr^{VI} compounds being the most toxic and carcinogenic compounds (in contrast to metallic chromium, Cr^{II}, and Cr^{III} compounds). For unknown reasons, the cation of chromates plays an important role in their toxicity: Although strontium compounds are generally not very toxic, strontium chromate is one of the most potent animal carcinogens ever identified.^[46]

Traces of heavy metals (As, Cd, Hg) are found in fireworks as a consequence of contaminated raw materials,^[41a] but they do not contribute significant amounts to the total emission and deposition of these elements within the country (Sweden, in a case study).

Military propellants based on beryllium fuels disperse potent carcinogenic beryllium aerosols and can be regarded as severe sources of pollution, despite of their good performance.^[5]

In terms of green chemistry, MTV and Al-Teflon/Viton mixtures or similar compositions are superior to other pyrotechnics because of the poor solubility in water and resulting low bioavailability^[47] of both the components and the combustion products (MgF₂, AlF₃). The environmental compatibility of the Berger mixture using zinc or zinc oxide and hexachloroethane, however, is poor. These mixtures cause the formation of zinc chloride (more bioavailable, though sensitive to hydrolysis) and several organic chlorides (see Section 2.2.3).

3.2. Perchlorates

Many pyrotechnic devices (including rocket propellants) contain perchlorate (mainly potassium and ammonium perchlorate) as oxidizers.^[11,48] However, the ClO₄⁻ ion has been shown to be teratogenic and to have negative effects on

thyroid gland function.^[49] Continuous uptake of perchlorates competitively inhibits the uptake of iodide by the thyroid gland and thus can lead to hypothyroidism.^[50] The mechanism of microbial-driven perchlorate biodegradation has been object of intense research.^[51]

Groundwater contamination related to the production, handling, and use of perchlorate-containing solid rocket propellants and pyrotechnic compositions (such as road flares, that are widely used in the US in case of automotive breakdowns) has been identified as a widespread problem.^[52] The costs for remediation of perchlorate contaminated US ground water are expected to be in the billions of US dollars. This negative economic impact may jeopardize major US Department of Defense programs.^[53] Thus, especially in the US, a significant effort is currently being made to remove perchlorates from pyrotechnic compositions, rocket propellants, and signal flares. For example, most military aerial decoy flares use perchlorates as oxidizers.^[54] Some perchlorate-free compositions (using nitrate as an oxidizer) have been investigated,^[55] however, they proved to have a high sensitivity to electrostatic stimuli.

3.3. Polychlorinated Organic Compounds

The combustion of organic matter (charcoal, asphaltum, organic binders) in presence of chlorine (in the form of chlorates, perchlorates, PVC powder, organic, or inorganic chlorides) in pyrotechnics may cause the formation of traces of toxic chlorinated organic compounds, such as polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF).^[2,56] Copper also plays a key role in the formation and degradation of PCDD and PCDF by catalytic reactions.^[2,57] From this point of view, pyrotechnic devices with a blue flame color are potentially the most toxic with respect to PCDD and PCDF pollution.

Interestingly, Fleischer et al.^[2] conclude that fireworks contribute only marginally to the total amount of PCDD/F and can hence be regarded as harmless in this respect (complete absence of the most toxic 2,3,7,8-TCDD), whereas Dyke and Coleman^[56] found a fourfold increase of PCDD/F concentration in ambient air in the course of a night of fireworks and bonfires and suggest that fireworks are a “significant source of dioxins”.

3.4. Smoke and Particulate Matter

Except in cases, where the generation of smoke is a desired effect, smoke is a multifaceted problem in pyrotechnics. It is caused primarily by fuels, which are traditionally carbon or metal-based. The smoke clouds the air and obscures the firework it also causes health problems, beyond the irritation of the spectators' eyes and noses. Several studies have investigated the release of inhalable particulate matter (PM; below 10 µm in diameter, PM₁₀) from fireworks and possible resulting health threats.^[58] Ravindra et al. noted a slight increase in PM₁₀ during the Diwali festival in India—probably an effect of the fireworks. The national Indian limits

for PM₁₀, however, were exceeded even before the beginning of the festival. Two other studies from Germany (Mainz and Leipzig)^[58b-c] showed a much more dramatic increase of the PM concentration compared to average ambient conditions following firework displays.

The launch of an AP/aluminum solid rocket produces tremendous amounts of hydrogen chloride, aluminum oxide, and aluminum chloride. The environment around rocket launch sites is severely affected by this pollution.^[59] In Kazakhstan, large areas are polluted with unburned, 1,1-dimethylhydrazine (unsymmetric dimethyl hydrazine, UDMH) fuel, because of the launch of Proton rockets at the Baikonur Cosmodrome.^[60] Like hydrazine, UDMH is toxic and probably carcinogenic. The oxidizer of this liquid propellant is dinitrogen tetroxide or eventually red fuming nitric acid (RFNA).

For the military, the development of smoke-free propellants is of major tactical importance, because the plume of (conventional) missile propellants can be detected easily by satellites. A smoke-free propellant producing N₂ only would therefore be desired to impede counteractive measures and to make an undetected strike possible.

3.5. Gaseous Pollutants

Pyrotechnics are potent sources of gaseous pollutants, as well.^[38,58c] Although these are less persistent than heavy metals or PCDD/PCDF, they are of interest, because, in case of a firework, they inconvenience the spectators' and the general population under unfavorable wind conditions. The main gaseous pollutants are CO, NO_x, and SO_x, and they cause immediate adverse health effects. In an early study, a statistically significant number of adults was observed to suffer chronic respiratory diseases (asthma) under the influence of firework pollution.^[36b] This observation is in good agreement with Murty^[37b] who reported an increase in the number of asthma patients by about 12 per cent in the course of the Diwali festival.

The sulfur content of gunpowder makes it the main source of SO_x. To a minor extent, sulfides, which are occasionally used as fuels, can also contribute to this pollution. NO_x is formed partly as the result of the oxidation of ambient N₂ at the high temperatures reached by burning metal fuels, as well as decomposition of nitrates.

4. Nitrogen-Rich Compounds: The Greening of Pyrotechnics

Novel developments in pyrotechnics focus on the application of nitrogen-rich compounds. In contrast to conventional energetic materials, this class of substances does not gain its energy from oxidation of a carbon backbone or a fuel but rather from high heats of formation. For pyrotechnics, these high-energy-density materials serve as potential propellants, coloring agents, and fuels—eventually in combination with less-toxic metal ions such as Cu^{II} instead of Ba^{II}. Nitrogen-rich materials combine several advantages:^[61]

- only or mostly gaseous products (smokeless combustion)
- high heats of formation
- high propulsive power
- high specific impulse
- high flame temperatures

“Green” pyrotechnics should primarily avoid perchlorates and heavy metals. Compounds applicable in fireworks should be cheap, easy to synthesize, and non-hygroscopic. A high nitrogen content is desirable for reduction of smoke and particulate matter. The reaction rate must be adjusted for the respective purpose. High-energy reactions are generally classified as “burning” (approximate reaction velocity in the range of mm or cm s⁻¹), “deflagration” (ms⁻¹) or “detonation” (km s⁻¹).

In energetic materials publications, acronyms are very common. Unfortunately, some of them are used inconsistently or are not self explanatory, giving rise to confusion. Therefore, a short overview of the most important pyrotechnic substances and their acronyms is given in Table 4.

Table 4: A selection of prevalent acronyms in pyrotechnics.

Acronym	Explanation
5-AT	5-aminotetrazole
ADN	ammonium dinitramide
AG	aminoguanidine
AN	ammonium nitrate
ANAT	3-amino-6-nitroamino-1,2,4,5-tetrazine
AP	ammonium perchlorate
BDDT	3,6-bis-(3,5-dimethylpyrazol-1-yl)-1,2-dihydro-1,2,4,5-tetrazine
BDT	3,6-bis-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine
BT	5,5'-bistetrazole
BTA	<i>N,N</i> -bis(1(2) <i>H</i> -tetrazol-5-yl)-amine
DAAT	3,3'-azobis(6-amino-1,2,4,5-tetrazine)
DAATO3.5	heptahemi- <i>N</i> -oxides of 3,3'-azobis(6-amino-1,2,4,5-tetrazine)
DAG	diaminoguanidine
DHT or Hz ₂ Tz	3,6-dihydrazino-1,2,4,5-tetrazine
DiAT	3,6-diazido-1,2,4,5-tetrazine
DN	dinitramide
G	guanidine
GAP	glycidyl azide polymer
GN	guanidinium nitrate
HNF	hydrazinium nitroformate
HTPB	hydroxyl-terminated polybutadiene
Hz or H	hydrazine
MIC	metastable intermolecular composites
MTV	magnesium/Teflon®/Viton® composition
NC	nitrocellulose
NF	nitroform
NG	nitroglycerine
NQ	nitroguanidine
TAG	triaminoguanidine
TAGN	triaminoguanidinium nitrate
TATTz or H3T	triazolo-aminotriazinyl-1,2,3,5-tetrazine
Tz	tetrazine
zT (or AT)	5,5'-azotetrazolate

4.1. Tetrazoles

Tetrazoles are unsaturated five-membered heterocycles containing four nitrogen atoms. The unsubstituted molecule CH_2N_4 has a nitrogen content of almost 80 wt %. The tetrazole ring system is aromatic and thus relatively stable.

Usually, it is the derivatives of tetrazole that are the objects of investigation for pyrotechnic purposes (see Sections 4.1.1–4.1.4), but the unsubstituted tetrazolate ion can also be made use of. A new smokeless pyrotechnic composition containing strontium ditetrazolate pentahydrate (Figure 2) as the coloring agent was recently developed in

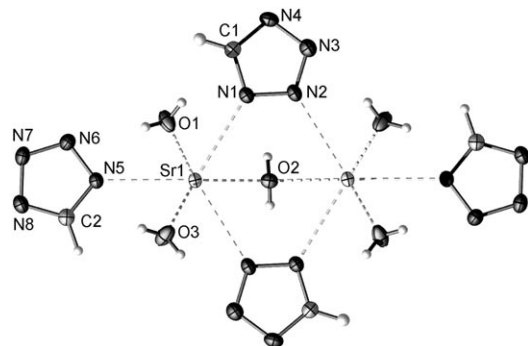


Figure 2. Extended molecular structure of strontium ditetrazolate pentahydrate.

our laboratory.^[62] Neither the formulation nor any of its individual ingredients show any impact, friction, or electrostatic sensitivity. The visible color is a bright red (Figure 3) originating from the SrOH molecule. The hydrogen needed to form the SrOH presumably comes primarily from the water of crystallization (Table 2).

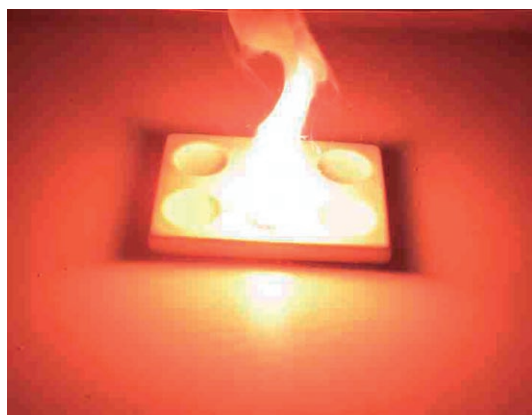


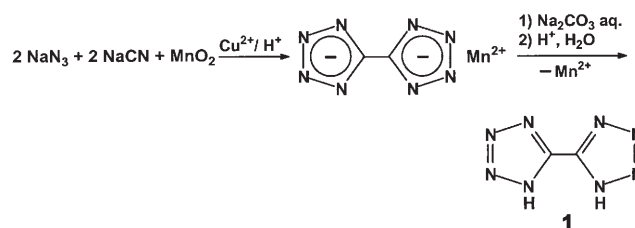
Figure 3. Bright red emission from a new smokeless pyrotechnic composition containing strontium ditetrazolate pentahydrate.

4.1.1. Bistetrazoles

5,5'-Bistetrazole (BT) is a diprotic acid that can be deprotonated by amines, metal carbonates, or hydroxides. Energetic salts of BT are frequently used and investigated as

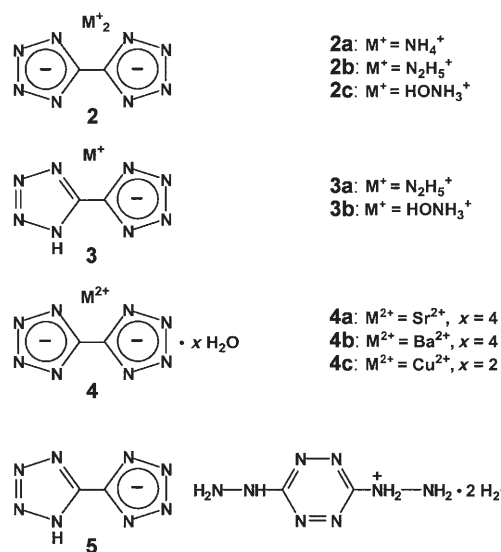
energetic materials.^[1] Reported pyrotechnic applications of BT and N,N -bis(1(2)*H*-tetrazol-5-yl)-amine (BTA) include the preparation of nanoporous metal foams (as discussed below), both anions are also excellent ligands for the preparation of nitrogen-rich complexes and salts.^[26,63–65] Furthermore, some of these compounds have been suggested for use in gas generators, automotive airbags, and as rocket-propellant additives in combination with AP or AN.

BT (**1**) is synthesized from sodium cyanide and sodium azide in aqueous solution upon the addition of manganese dioxide and a mixture of sulfuric acid, glacial acetic acid, and Cu^{II} ions as a catalyst. The acid **1** is freed from the resulting Mn -BT salt in a buffered carbonic acid solution (Scheme 1).^[26,66] Although the free acid is quite sensitive



Scheme 1.

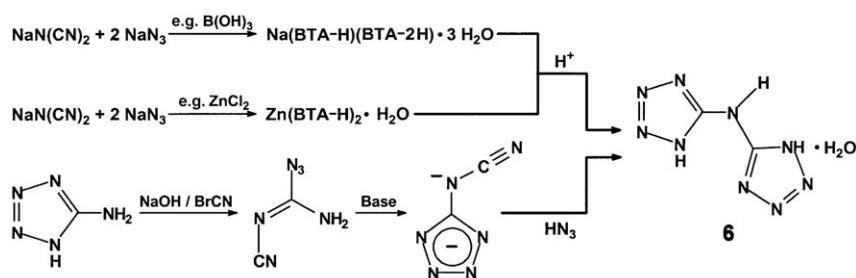
(drop-hammer sensitivity 3.75 J), its salts are usually much less sensitive. Several have been synthesized in aqueous solution by Chavez et al.^[26] from BT and bases (amines or metal hydroxides, unless otherwise noted). Characterization was performed by elemental analysis and partly by ^{13}C NMR spectroscopy and thermogravimetric analysis (TGA). They synthesized the following compounds: diammonium 5,5'-bis-1*H*-tetrazolate (**2a**), dihydrazinium-BT (**2b**), dihydroxylammonium-BT (**2c**), hydrazinium-BT (**3a**), hydroxylammonium-BT (**3b**), strontium-BT tetrahydrate (**4a**), barium-BT tetrahydrate (**4b**), copper(II)-BT dihydrate (**4c**; synthesized



from BT and copper(II) sulfate pentahydrate in aqueous solution), and 3,6-dihydrazino-1,2,4,5-tetrazinium-BT (**5**). The salts **4a–c** are promising coloring agents for red and green pyrotechnic effects. Although the barium salt **4b** is definitely not a “green” compound, it had been investigated because of its smokeless combustion. Although **4a–c** lose crystal water when heated, they are sufficiently thermally stable (to over 100 °C). The 5,5'-bistetrazolates of ammonium, hydrazinium and hydroxylammonium (**2–3**) show variable performance: **2b** is a poor fuel, because it melts and decomposes before it catches fire, whereas **2a** has acceptable properties for applications, for example, as a gas-generating agent for airbags.

4.1.2. Bistetrazoleamines

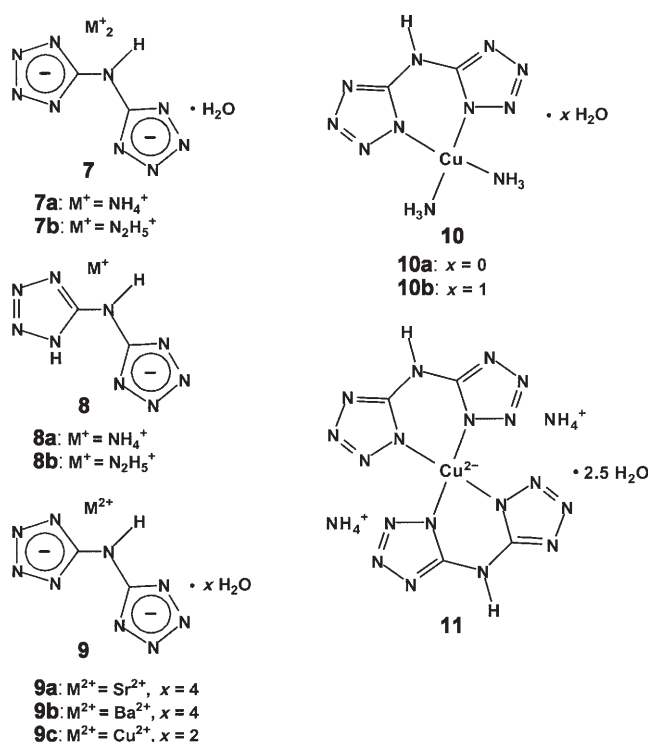
The diprotic acid *N,N*-bis(1(2)*H*-tetrazol-5-yl)-amine monohydrate (BTaw, **6**) can be obtained from three different syntheses,^[67] as shown in Scheme 2. One straightforward reaction is based on the use of sodium dicyanamide, sodium azide, and a catalyst such as zinc chloride, bromide or perchlorate, followed by acidic work-up (Scheme 2, middle).^[68] Another simple synthesis also uses inexpensive sodium dicyanamide, sodium azide and a weak acid such as trimethylammonium chloride, boric acid, ammonium chlo-



Scheme 2.

ride,^[69] or slow addition of hydrochloric acid (Scheme 2, top).^[70] In a different approach, 5-aminotetrazole is treated with cyanogen bromide under base-catalyzed conditions. The intermediate compound undergoes a cycloaddition when treated with azide under acidic conditions (hydrazoic acid; Scheme 2, bottom).^[71]

The monohydrate BTaw is impact insensitive (< 80 J), but the dehydrated form BTA exhibits a dramatically increased drop-hammer sensitivity (6.5 J). Several compounds of BTA have been synthesized and characterized (by elemental analysis and partly by ^{13}C NMR spectroscopy and TGA)^[26] and investigated with respect to their applicability as a pyrotechnic fuel, these include: diammonium bis-(1(2)*H*-tetrazol-5-yl)-amine monohydrate (**7a**), dihydrazinium-BTA monohydrate (**7b**), ammonium-BTA (**8a**), hydrazinium-BTA (**8b**), strontium-BTA tetrahydrate (**9a**), barium-BTA tetrahydrate (**9b**), and copper(II)-BTA dihydrate (**9c**). As in the case of 5,5'-bistetrazolates mentioned in Section 4.1.1, synthesis was performed from the free acid **6** and bases, such as amines, strontium and barium hydroxide, and



copper(II) sulfate solution. We have investigated some promising copper(II) BTA complexes:^[64] $[\text{Cu}(\text{BTA})(\text{NH}_3)_2]$ (**10a**), $[\text{Cu}(\text{BTA})(\text{NH}_3)_2] \cdot \text{H}_2\text{O}$ (**10b**), and $[(\text{NH}_4)_2\text{Cu}(\text{BTA})_2] \cdot 2.5 \text{H}_2\text{O}$ (**11**). Complex **10a** is prepared from concentrated aqueous solutions of BTaw, copper(II) chloride dihydrate, and ammonia, **10b** under similar conditions but with excess water, and **11** by addition of diluted ammonia. **10a,b** and **11** are fully structurally characterized by X-ray crystal-structure analysis, indicating the variable coordination modes of the BTA^{2-} ion. Furthermore, IR spectroscopy, elemental analysis, differential scanning calorimetry (DSC), TGA measurements, and bomb calorimetry have been carried out.^[64] The explosive and magnetic properties of the compounds have been determined as well.^[64] The application of **10a** and **11** as additives in pyrotechnics and AP-based propellants has been suggested because of their favorable properties (bright emission of colored light and low sensitivity) and the inexpensive starting materials.

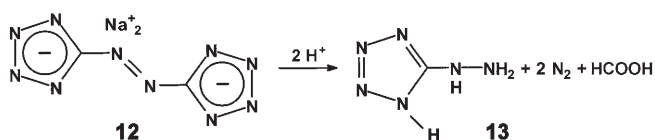
An interesting technical application of pyrotechnics has been developed in the Los Alamos National Laboratory: the synthesis of nanostructured metal foams by combustion of BTA complexes.^[63,72] Under inert atmosphere, these compounds decompose upon ignition and through unusual combustion and redox chemistry, the metal ion is reduced giving a highly nanovesicular foam. As a result of their properties (such as low density, large specific surface, high stiffness, gas permeability), these materials find application in catalysis, fuel cells, and hydrogen storage as well as thermal and acoustic insulation. The authors from Los Alamos present

several metal complexes of BTA used for this purpose and discuss the resulting materials. In particular, metal foams of iron, cobalt, copper, and silver have been produced by combustion of the respective BTA-complexes.

4.1.3. Azotetrazoles

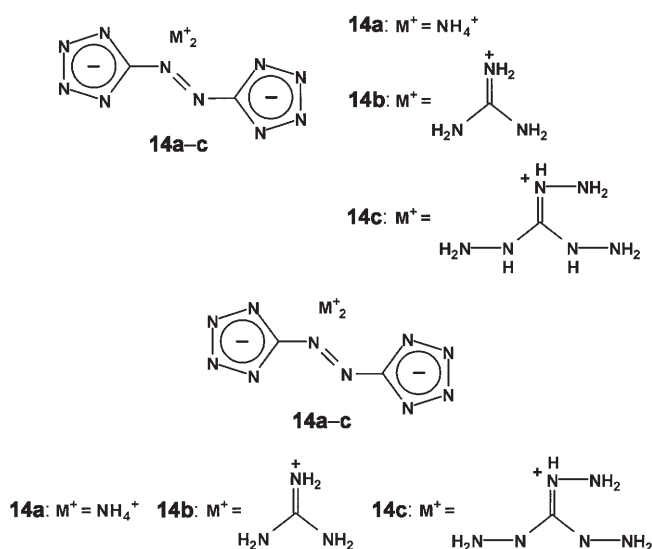
Of all of the promising bistetrazoles for pyrotechnic applications, the 5,5'-azotetrazolate anion has the highest nitrogen content (85.4%). In many cases, azotetrazolate salts have a higher sensitivity than the respective BT or BTA compounds, especially after removal of crystal water. Azotetrazolates may find application as primary or secondary explosives^[73] or gas generators.^[1]

5,5'-Azotetrazolate is synthesized as the sodium salt **12** by oxidation of 5-aminotetrazole under oxidizing and basic conditions (KMnO₄, NaOH).^[1,74] The free acid 5,5'-azotetrazole can be obtained only under special conditions.^[73] It undergoes acidic decomposition with mineral acids, forming hydrazinotetrazole (**13**), dinitrogen, and formic acid (Scheme 3). Azidotetrazole, 5-azo(diazomethano)tetrazole hydrate, and other compounds were recovered as intermediates or by-products of this decomposition.^[75]



Scheme 3.

Several salts of 5,5'-azotetrazolate have been suggested for pyrotechnic applications. In particular, ammonium- (**14a**), guanidinium- (**14b**), and triaminoguanidinium-5,5'-azotetrazolate (**14c**) were investigated.^[63,76] Compounds **14a** (979 mL of gas per gram) and **14c** (981 mL of gas per gram) are viable candidates for smokeless gas generators. In contrast, **14b** was found to burn with some smoke production. However, its application as propellant additive appears very promising.

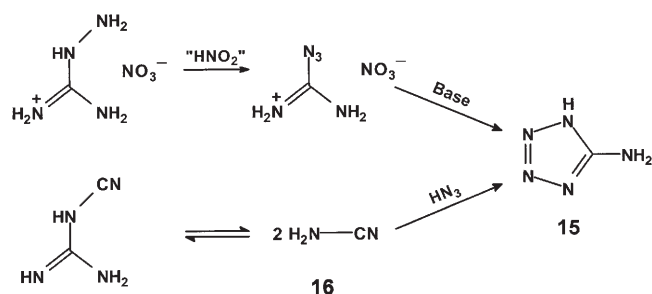


Compound **14c** has exceptionally fast low-pressure burning rates.^[77] All compounds **14a-c** have been characterized by NMR spectroscopy and crystal-structure analysis.^[76a] In the search for new hybrid rocket fuels, it was found that **14b** reacts with the N100 curative in hydroxy-terminated polybutadiene (HTPB), but not with polyisocyanate (PAPI) curative. When used as an additive, **14b** increases the regression rate of HTPB, the regression rate is a measure of how much of the solid fuel is burning in a given time.^[76b] This propellant was shown to perform very well with respect to thrust and resulting pressure in tests at the hybrid rocket motor facility at University of Arkansas at Little Rock and its performance was also within safe operating parameters.

By grinding with the right amount of ammonium nitrate, compositions of **14a** can be oxygen balanced. The mixtures are candidates for application as explosives, which offer low cost, minimal smoke production and—surprisingly—even lower impact sensitivity than pure ammonium nitrate.^[76a]

4.1.4. Aminotetrazoles

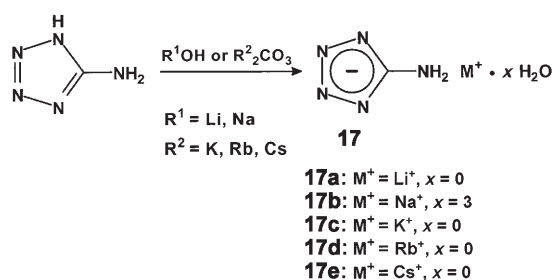
5-Aminotetrazole (**15**) is a valuable starting material for the syntheses of many tetrazole derivatives. It is synthesized either from aminoguanidinium nitrate with nitrous acid and basic work-up^[78] or in a reaction of cyanamide (**16**) with hydrazoic acid^[79] (see Scheme 4).



Scheme 4.

In a recent paper, the properties and crystal structures of the alkali-metal salts (**17a-e**) of the 5-aminotetrazolate anion have been presented and discussed.^[80] The lithium and sodium salts are synthesized from the respective hydroxides, the potassium, rubidium, and cesium salts from the corresponding carbonates and aqueous solutions of **15** (Scheme 5).

Only the sodium salt **17b** crystallizes with three molecules of water. The sodium ion is coordinated by one nitrogen atom of the tetrazole ring and five water molecules. The cations of the other compounds are coordinated by several nitrogen atoms of the ring and the amino group. Compounds **17a-e** were investigated by NMR spectroscopy, elemental analysis, DSC, bomb calorimetry, and vibrational (IR and Raman) spectroscopy. The compounds are synthesized from inexpensive raw materials in almost quantitative yield and are thermally stable up to 350°C. They melt without decomposition. The flame colors are red (**17a**), orange (**17b**), purple (**17c**), lavender (**17d**), and pink (**17e**). All the compounds are very promising for the application in fireworks or flares. The



Scheme 5.

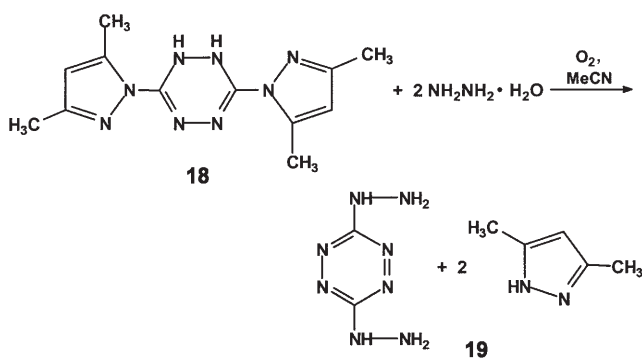
lithium compound could serve in perchlorate-free pyrotechnics with a red flame color. Despite their high nitrogen content, all the compounds have low friction and impact sensitivities.

4.2. Tetrazines

Tetrazines are aromatic six-membered rings with four nitrogen atoms in the 1,2,4,5- or 1,2,3,5-positions. Tetrazines (nitrogen content of $\text{C}_2\text{H}_2\text{N}_4$:68.3%) have high heats of formation and high crystal densities. Both are important and desirable features for energetic materials.^[1] One of the most famous tetrazine derivative is the high explosive LAX-112 (3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide).^[66]

4.2.1. Dihydrazino- and Diazido Tetrazine

One of the most promising materials for smokeless colored pyrotechnics is 3,6-dihydrazino-1,2,4,5-tetrazine (**19**, DHT or Hz_2Tz). The compound has been known since the work of Marcus and Remanick in 1963,^[81] who applied hydrazinolysis to 3,6-diaminotetrazine. Some decades later, an improved synthesis with a high yield was published, which is based on readily available **18** (BDDT) and hydrazine under oxidizing conditions (see Scheme 6).^[82] Compound **18** is a precursor in the production of LAX-112. It is synthesized from triaminoguanidinium chloride and 2,4-pentanedione.^[66,82a,83] The product was characterized using ^1H and ^{13}C NMR spectroscopy. The thermal decomposition of DHT has been extensively investigated. In the first principal step, nitrogen is eliminated from the tetrazine ring followed by

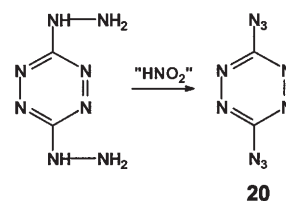


Scheme 6.

cleavage of the remaining N–N bond, and loss of the substituent group.^[84] The burning rate of DHT has been measured—it is substantially faster than the conventional propellant HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and the pure material is nearly as pressure sensitive. Upon addition of a little binder, the pressure dependence can be significantly reduced. DHT burns with very little luminosity in the gas phase and much lower temperatures than HMX.^[85]

Pyrotechnic stars can be obtained by grinding DHT with an oxidizer (AN or AP) and a small amount of a colorant (such as, sodium (yellow), strontium (red), or barium nitrate (green), copper(II) oxide or sulfide (both blue)^[86] or antimony(III) sulfide (white)). These mixtures are also interesting because they do not need a binder; they are simply moistened with water or ethanol (in case of ammonium nitrate based mixtures), pressed in shape, and air dried. A small amount of AP is needed in AN-based formulations to act as chlorine source, which is necessary to obtain brilliant colors. Some of the mixtures show variable impact sensitivity, which also depends on relative humidity—humid weather decreases the sensitivity.^[26] Furthermore, DHT has been suggested for application in gun or rocket propellants.^[66] A significant drawback of DHT is the toxicity of the hydrazine moiety in the molecule.

A derivative of DHT, 3,6-diazido-1,2,4,5-tetrazine (**20**, DiAT) is produced from DHT and nitrous acid (see Scheme 7).^[63] DiAT is far too sensitive to find application as

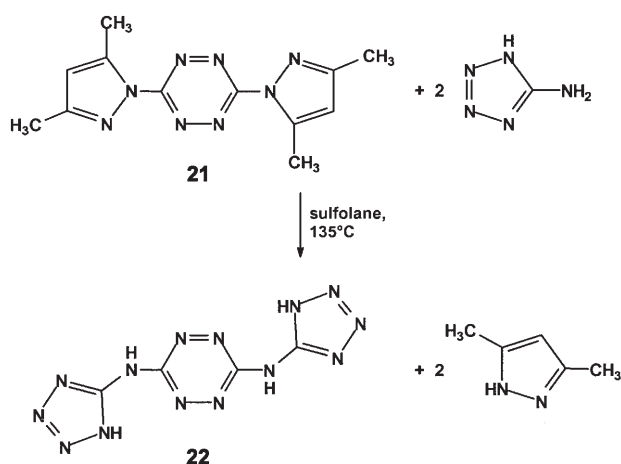


Scheme 7.

a pyrotechnic component in the traditional sense. However, Chavez et al. discuss the preparation of carbon and carbon nitride nanoparticles by pyrolysis of DiAT, such nanoparticles find many applications in several technological fields. The carbon nitrides with variable nitrogen content (C_3N_4 and C_3N_5) were identified using IR spectroscopy and elemental analysis. The carbon nanospheres range from 5–50 nm in diameter; the carbon nitrides show various morphologies.

4.2.2. Bistetrazolylamino-s-tetrazine

By oxidation using atmospheric oxygen or nitrogen dioxide, two hydrogen atoms are abstracted from **18**, forming **21** (BDT), which is also the first reaction step in the synthesis of DHT. BDT reacts with 5-aminotetrazole at elevated temperatures, forming **22** (BTATz; Scheme 8).^[63,66,87] This compound, combining the 1,2,3,4-tetrazole and the 1,2,4,5-tetrazine ring systems, has a nitrogen content of almost 80% and a high heat of formation ($+883 \text{ kJ mol}^{-1}$), it is thermally



Scheme 8.

quite stable (DSC onset of 264°C). It would be a viable candidate for use in high-performance propellants but pure BTATz is fairly sensitive to spark initiation (0.36 J). However the addition of a small amount of binder can greatly reduce the sensitivity to electrostatic discharge. Pure **22** has an impact sensitivity of 8 J and is not friction sensitive. Its combustion properties have been determined with regard to a possible application as a propellant or for use on existing micropropulsion designs.^[88] It burns at 6.89 MPa with an unusually fast rate (4.6 cm s⁻¹), comparable to TAGzT (4.9 cm s⁻¹). Unfortunately, the burning rate exhibits a relatively high dependence on pressure.^[63,85,89]

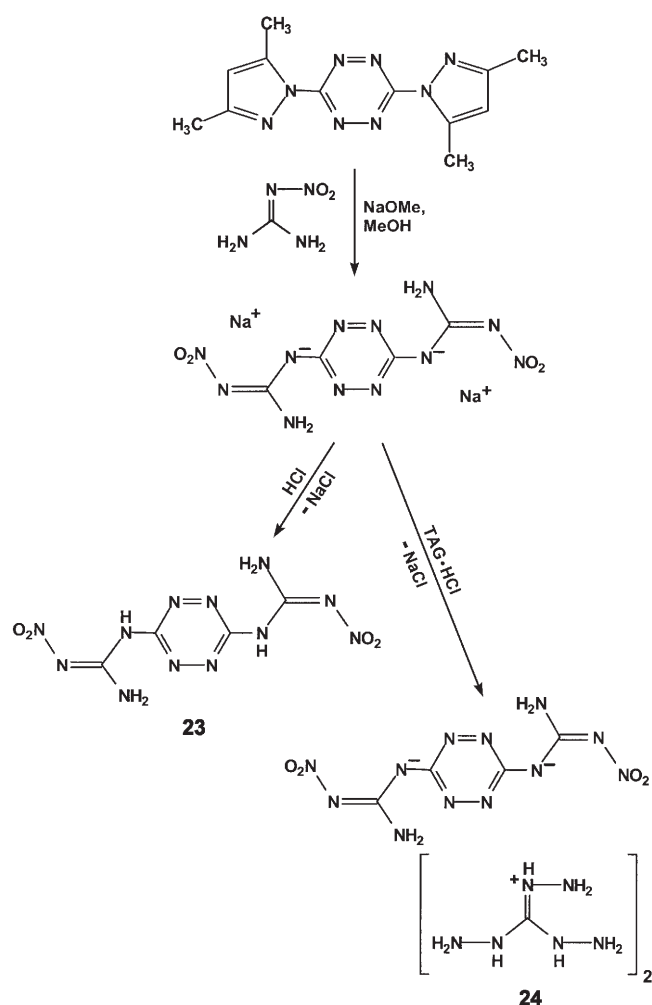
4.2.3. Nitroguanyltetrazines

At the Los Alamos National Laboratory, two energetic nitroguanyltetrazine compounds have been synthesized and presented for use in pyrotechnics: 3,6-bis-nitroguanyl-1,2,4,5-tetrazine (**23**, (NQ)₂Tz) and its triaminoguanidinium salt (**24**, (TAG)₂(NQ)₂Tz).^[63,90] The high-yield synthesis is accomplished from BDT and two equivalents of nitroguanidine (or its sodium salt; Scheme 9). Treatment of the disodium intermediate with triaminoguanidinium chloride leads to the formation of **24**, which has an exceptionally high heat of formation of 1255 kJ mol⁻¹.

The DMSO adduct of **23** has been characterized structurally,^[90a] demonstrating that (NQ)₂Tz exists in the nitrmino form. The burning rates at 6.89 MPa are 2.0 (**23**) and 2.3 cm s⁻¹ (**24**), respectively, are reasonable and the pressure dependence of the burning rates is very low. Both materials might thus find application in gas generators, high explosives (calculated detonation velocities > 7.5 km s⁻¹), or as additives in propellants. Compound **24** is less thermally stable (DSC onset 166°C) than **23** (228°C). (NQ)₂Tz has a higher impact sensitivity, both substances are not friction sensitive.

4.2.4. Azobistetrazines

In contrast to 5,5'-azotetrazolates, 3,3'-azobistetrazines cannot be obtained by direct oxidation of a 3-aminotetrazine, this approach leads to *N*-oxides (oxide α to the amino

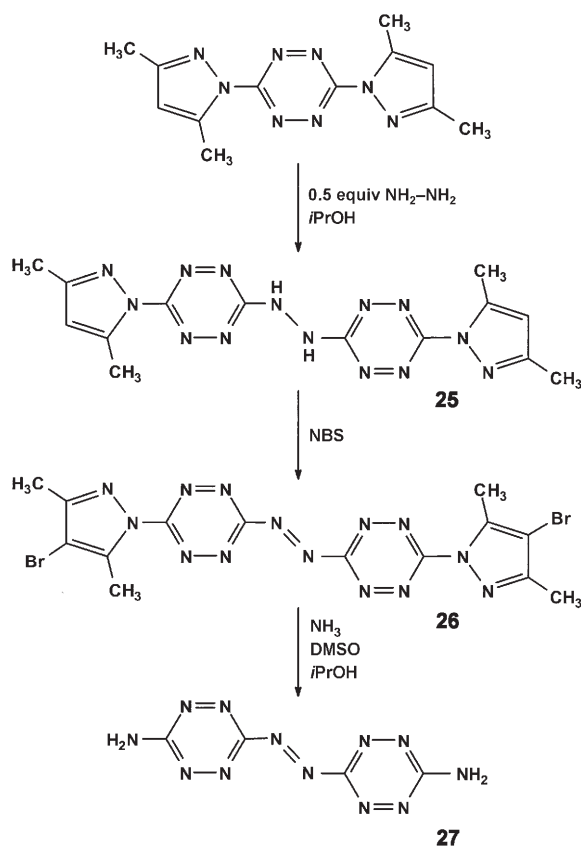


Scheme 9.

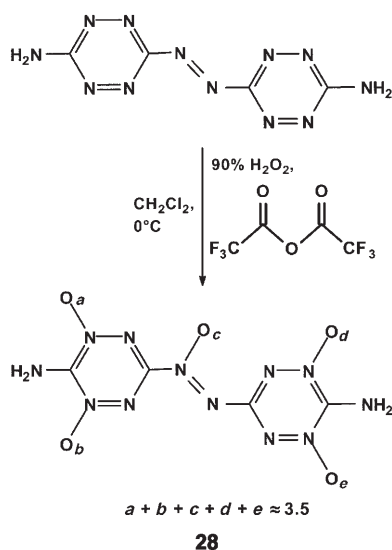
group).^[91] In an alternative synthetic route, BDT is treated with hydrazine; the resulting hydrazo compound **25** is oxidized using *N*-bromosuccinimide (NBS). By further treatment with ammonia in DMSO and 2-propanol, the 4-bromo-3,5-dimethylpyrazol-1-yl groups of **26** can be replaced quantitatively, forming **27** (DAAT; Scheme 10).^[92]

The crystal structure of the bis(DMSO) solvate of **27** could be determined. The pure compound is thermally stable to 252°C, it is hardly friction (324 N) or spark sensitive, and the impact sensitivity value is 5 J. Compound **27** has a high heat of formation (+862 kJ mol⁻¹, in a later bomb calorimetry measurement: +1035 kJ mol⁻¹). DAAT exhibits a graphite-like structure, giving an extremely high density of 1.84 g cm⁻³ (later determined to 1.76 g cm⁻³, using gas pycnometry). It was characterized by NMR and IR spectroscopy and TG-MS was used to analyze its decomposition gases.^[92c]

The oxidation of DAAT with peroxytrifluoroacetic acid (generated in situ) (Scheme 11) leads to a mixture of *N*-oxides, given the acronym DAATO3.5 (**28**).^[87] By fractional recrystallization, 3,3'-azobis-(6-amino-5-*N*-oxide-1,2,4,5-tetrazine) could be isolated and identified by crystal structure analysis ($a = e = 1$; $b = c = d = 0$).



Scheme 10.



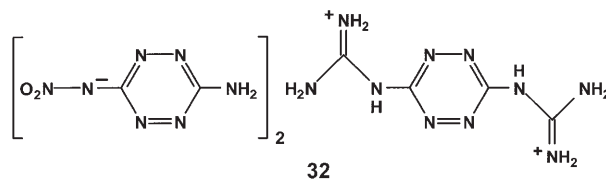
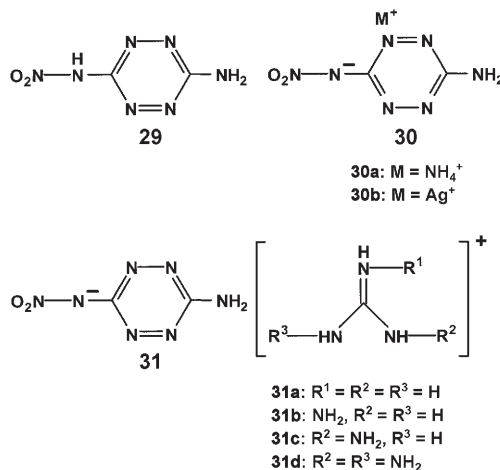
Scheme 11.

^{13}C NMR spectroscopy was used to gain insight into the complexity of the mixtures of *N*-oxides, the average oxygen content was determined using elemental analysis to be approximately 3.5 atoms per molecule. Taking into consideration that it is a mixture of compounds, DAATO3.5 has a very high density (1.88 g cm^{-3}), a variable but considerable sensitivity to friction, impact, and sparks.^[63] By using a binder, these sensitivities can be diminished. The most outstanding

feature of this material is its high burning rate (5.4 cm s^{-1}), reported to be the highest of any known organic solid.^[89] Very desirably, the pressure dependence of the burning rate is very low, which is a prerequisite for applications as a propellant ingredient.

4.2.5. Salts of 3-Amino-6-nitroamino-*s*-tetrazine

Another potential propellant constituents are compounds based on 3-amino-6-nitroamino-1,2,4,5-tetrazine (ANAT). Several energetic ANAT salts have been published recently; the free acid **29**, and the corresponding salts of ammonium

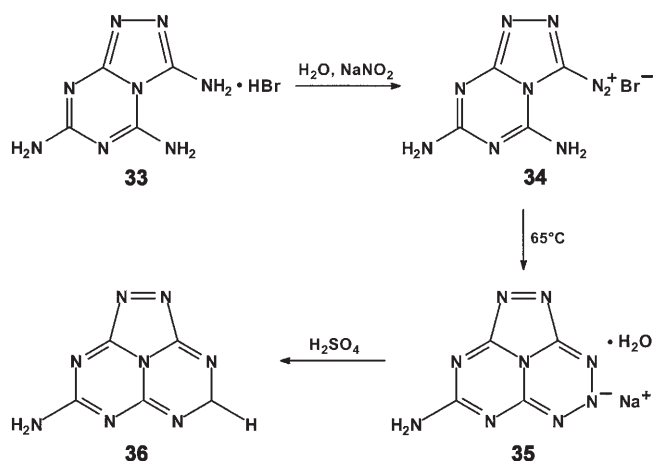


(**30a**), silver (**30b**), guanidinium (**31a**), mono-, di-, and triaminoguanidinium (**31b–d**), and 3,6-diguanidine tetrazine (**32**).^[93] Synthesis of salts is performed from the free bases or from the corresponding carbonates or via the silver salt **30b** and the corresponding chlorides (metathesis reaction).

The crystal structure of **31a** has been determined by X-ray diffraction, all the salts were characterized by IR, NMR spectroscopy and elemental analysis.

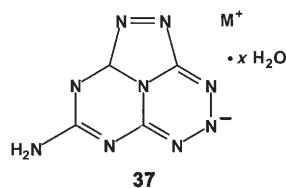
4.2.6. Triazoloaminotriazinyl-1,2,3,5-tetrazine and Related Salts

An example of a compound with an interesting 1,2,3,5-tetrazine ring system is triazolo-aminotriazinyl-1,2,3,5-tetrazine (**36**, H3T or TATTz) and salts thereof. Synthesis of **36** is performed as follows: 2-hydrazino-4,6-diaminotriazine is treated with BrCN to give **33** as the hydrobromide salt. Treatment of an aqueous suspension with sodium nitrite gives the intermediate diazonium salt **34**. Heating to 65°C leads to the formation of the sodium salt **35** in the form of red crystals, which can be transformed to the free acid **36** (yellow powder) by treatment with diluted sulfuric acid (see Scheme 12).^[94]



Scheme 12.

TATTz was the first 1,2,3,5-tetrazine with a pure CHN composition and the first fused 1,2,3,5-tetrazine. It has a density (determined by gas pycnometry) of 1.77 g cm^{-3} . Thermal decomposition occurs at 213°C . The free acid is sensitive to impact, friction, and electric discharge, whereas the corresponding salts are much less sensitive. Koppes et al. reported the synthesis and characterization of the ammonium (37a), hydrazinium (37b), dihydrazinium-1,2,4,5-tetrazinium (37c), diaminoguanidinium (37d), triaminoguanidinium (37e), and the guanyl urea salts (37f), as well as the inorganic salts with Al^{III} , Co^{II} , Ni^{II} , Cu^{II} , and Ba^{II} cations (37g–k).^[94]



37a: $\text{M}^+ = \text{NH}_4^+$, $x = 0$

37b: $\text{M}^+ = \text{N}_2\text{H}_5^+$, $x = 0$

37c: $\text{M}^+ = \text{H}_2\text{N}-\text{H}_2\text{N}-\text{N}^+=\text{N}-\text{NH}_2$, $x = 0$

37d: $\text{M}^+ = \text{H}_2\text{N}-\text{C}(=\text{NH}-\text{NH}_2)-\text{NH}-\text{NH}_2$, $x = 0$

37e: $\text{M}^+ = \text{H}_2\text{N}-\text{HN}-\text{C}(=\text{NH}-\text{NH}_2)-\text{NH}-\text{NH}_2$, $x = 0$

37f: $\text{M}^+ = \text{H}_2\text{N}-\text{C}(=\text{O})-\text{NH}-\text{C}(=\text{NH}_2)-\text{NH}_2$, $x = 1$

37g: $\text{M}^+ = \text{Al}^{3+}/3$, $x = 7.5$

37h: $\text{M}^+ = \text{Co}^{2+}/2$, $x = 6$

37i: $\text{M}^+ = \text{Ni}^{2+}/2$, $x = 6$

37j: $\text{M}^+ = \text{Cu}^{2+}/2$, $x = 5$

37k: $\text{M}^+ = \text{Ba}^{2+}/2$, $x = 7$

Synthesis was performed either by acid–base reactions or by cation exchange. All compounds were characterized by elemental analysis and, where applicable, NMR spectroscopy. The crystal structure of 37f was also determined.^[94b] Koppes et al suggest application of these materials in pyrotechnics, gas generators, propellants, and explosives. Compound 37e has been tested in a gun-propellant formulation showing good performance. Unfortunately, no reports on the flame colors of 35, 37j, and 37k are given.

4.3. Guanidines

Guanidine ($(\text{H}_2\text{N})_2\text{C}=\text{NH}$) is a nitrogen-rich compound. The free base as well as an interesting guanidinium nitroguanidinium bisnitrate have been characterized structurally only recently.^[95] Guanidinium salts are synthesized from cyanamide or dicyandiamide by addition of ammonium salts. Derivatives of guanidine, that is, mono-, di-, and triaminoguanidines and nitroguanidines and salts thereof, have many applications as energetic materials or gas generators.^[1]

In pyrotechnics, guanidinium nitrate has been applied as an energetic additive for decades. Similarly, nitroguanidine has a long history as constituent of triple-base propellants (see Section 2.5.).

Hiskey and Naud proposed the application of nitroguanidine, nitrocellulose, a flame coloring agent, an oxidizer, and a metal-powder fuel in pyrotechnic compositions for fireworks (stars, flares etc.).^[96] These pyrotechnics are reported to perform well and to burn with a minimum of smoke generation. Unfortunately, perchlorates were proposed as oxidizers, which reduces their “green” value.

Judge et al. discuss intensively the properties of a propellant for rockets and missiles based on glycidyl azide polymer/ammonium nitrate/triaminoguanidinium nitrate in two recent papers.^[97] The composite propellant proved good performance (burn rates comparable to typical solid propellant formulations now in service) and stability, despite some previous reports that triaminoguanidinium nitrate based propellants have raised concerns with respect to thermal stability and compatibility with other ingredients. The composition has a low toxicity and produces non-acidic exhaust gases.

4.4. Miscellaneous

4.4.1. Nitroformates

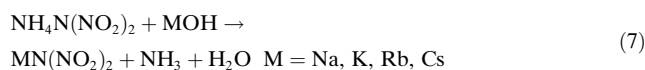
Salts of the strong acid trinitromethane are called nitroformates. The hydrazinium salt—hydrazinium nitroformate ($\text{H}_2\text{N}-\text{NH}_3^+ \text{C}(\text{NO}_2)_3^-$; HNF)—has already found practical application as a propellant oxidizer. However, HNF, its derivatives, and new nitroformates are still the objects of research.^[98] Triaminoguanidinium nitroformate (TAGNF), for example, shows high calculated values for the detonation pressure (330 kbar) and a higher volume of detonation products (885 L kg^{-1}) than HNF (826 L kg^{-1}). However, using several techniques, it was possible to significantly improve the properties of HNF with respect to its storage

properties, acceptable morphology, and stability.^[99] Unfortunately, hydrazine is a proven carcinogen substance, which disqualifies HNF as a “green” propellant to a certain extent.

4.4.2. Dinitramides

Ammonium dinitramide ($\text{NH}_4\text{N}(\text{NO}_2)_2$; ADN) is a very promising compound that may be utilized as an oxidizer in environmentally friendly spacecraft monopropellants.^[100] Some ADN-based propellant mixtures (with glycerol, glycine, methanol) showed not only high density but also higher specific impulse than hydrazine-based propellants. ADN is not carcinogenic and it has good stability and storage properties.

Amongst some other salts, the alkali dinitramide salts have been synthesized, characterized, and investigated for the application as pyrotechnic oxidizers.^[101,102] In a straightforward synthesis, ADN is treated with the desired alkali hydroxide in water or methanol [Eq. (7)].



The salts were fully characterized by elemental analysis, IR, DSC, TGA, melting-point determination, and X-ray crystal-structure analysis.^[101] In pyrotechnics, the salts offer high burning rates and specific impulse and little generation of smoke. However, in their report, Berger et al. do not comment on the flame color of the compounds or formulations.

The energetic properties of Ti/KDN and Ti/CsDN mixtures were intensively investigated in a recent study.^[102b] The mixtures show moderate sensitivity to friction or sparks, but they are highly sensitive to impact. Therefore, the investigation of these mixtures in ignition systems as environmentally benign primary explosives was suggested.

5. Outlook and Conclusion

It is clear from a vast array of studies that traditional pyrotechnics are a severe source of pollution. “Green” formulations are based on nitrogen-rich compounds which avoid heavy metals and perchlorates. Many attempts are currently underway to substitute copper for barium in pyrotechnics for green flame coloration. High-nitrogen compounds gain their energetic character not by oxidation of carbon but from their high heats of formation. They offer not only environmentally compatible combustion products, but in many cases even better color quality and intensity than older formulations. Their application in propellants provides better performance and truly smokeless combustion.

New oxidizers should avoid perchlorate because of its toxicity. A possible solution to this problem could be the introduction of nanometer-sized metal particles into the pores of nanostructured metal oxides—this is a true challenge for chemists. In many cases, perchlorate is added to a pyrotechnic mixture as a source of chlorine rather than an oxidizer. This field of chlorine donors thus offers room for improvements, as

well. With the development of suitable alternatives, the now widely used perchlorates may be abandoned in the future.

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