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Kirstin F. Warner[a]; Richard H. Granholm[a]
[a] Indian Head Division, Naval Surface Warfare Center, Indian Head, Maryland

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Synthesis of Insensitive 5,5′-Azotetrazolate Salts

KIRSTIN F. WARNER and
RICHARD H. GRANHOLM

Indian Head Division, Naval Surface Warfare Center,
Indian Head, Maryland

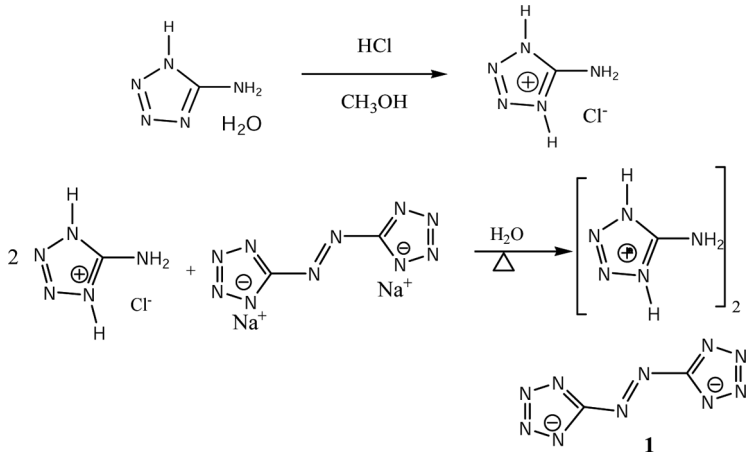
Salts of 5,5′-azotetrazolate with 5-aminotetrazole and 2,4,6-triamino-s-triazine cations were synthesized as potential ingredients for gun propellants. These salts were characterized by nuclear magnetic resonance (NMR) and infrared spectroscopy. Thermal properties were studied by differential scanning calorimetry (DSC). Their reactions to mechanical stimuli were also determined by small-scale sensitivity testing, small-scale shock reactivity testing, and small-scale internal blast testing.

Keywords: 5,5′-azotetrazolate salts, energetic salts, explosives, high nitrogen

Introduction

In recent years, there has been a great deal of interest in high nitrogen compounds [1–8]. A series of tests was performed to gain insight into their thermal stability, handling, and sensitivity and the explosive characteristics of these salts. These salts are potential ingredients for gun propellants and gas generators.

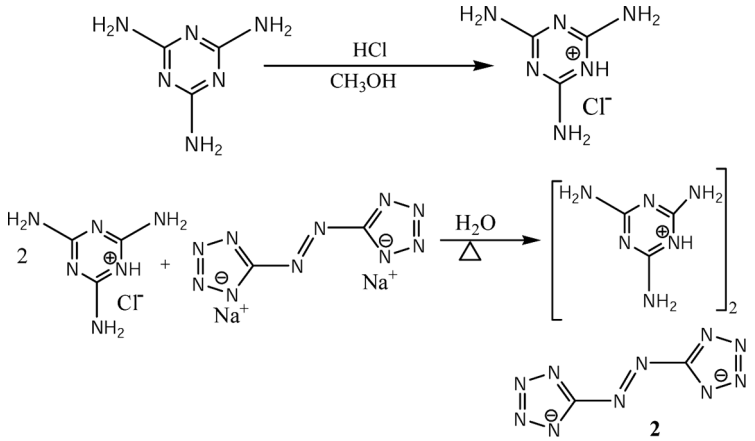
Address correspondence to Kirstin F. Warner, Indian Head Division, Naval Surface Warfare Center, 4104 Evans Way, Suite 102, Indian Head, MD 20640. E-mail: kirstin.warner@navy.mil



Scheme 1. Synthesis of 5-aminotetrazolium 5,5′-azotetrazolate.

This article addresses the synthesis and insensitivity of 5,5′-azotetrazolate salts with 5-aminotetrazole and 2,4,6-triamino-s-triazine cations.

5-Aminotetrazole monohydrate and 2,4,6-triamino-s-triazine are commercially available and were used as received. The corresponding hydrochloride salt was easily prepared by reacting



Scheme 2. Synthesis of 2,4,6-triamino-s-triazinium 5,5′-azotetrazolate.

5-aminotetrazole monohydrate or 2,4,6-triamino-s-triazine with 37% hydrochloric acid in methanol as shown in Schemes 1 and 2 [9]. The corresponding hydrochloride salt was allowed to react with sodium 5,5′-azotetrazolate in an aqueous solution to afford 5-aminotetrazolium 5,5′-azotetrazolate (**1**) and 2,4,6-triamino-s-triazinium 5,5′-azotetrazolate (**2**), respectively.

Results and Discussion

Differential scanning calorimetry (DSC) measurements were performed at 5°C/min in a nitrogen atmosphere at a flow rate of 50 mL/min. 5-Aminotetrazolium 5,5′-azotetrazolate (**1**) began to decompose at 134.3°C with a peak exotherm at 170°C. 2,4,6-Triamino-s-triazinium 5,5′-azotetrazolate (**2**) began to decompose at 248.3°C with a peak exotherm at 270°C. As shown in Table 1, the small-scale sensitivity data of (**1**) and (**2**) were in the low to medium sensitivity range for impact, friction, and electrostatic discharge compared to RDX with medium sensitivity.

Explosive behavior is summarized in Table 2. The small-scale shock reactivity test (SSRT) produces a dent, with its depth correlating with reactivity [10]. 5-Aminotetrazolium 5,5′-azotetrazolate produced a dent depth of 2.5 mm and an internal blast peak quasi-static overpressure (P_{QS}) of 15 psig,

Table 1
Small-scale sensitivity data

Material	ERL impact 50% hgt (cm)	ABL friction 20 TIL (psig)	ABL ESD 20 TIL (joules)	DSC onset/peak (°C)
5-aminotetrazolium 5,5′-azotetrazolate	178	180	0.326	134.3/270
2,4,6-triamino-s-triazinium 5,5′-azotetrazolate	100	≤560	≤0.095	248.3/270
Reference: RDX	21	135	0.165	212/235

Table 2
Small-scale shock reactivity and internal blast data

Material	Dent depth (mm)	P_{QS} (psig)
5-aminotetrazolium 5,5′-azotetrazolate	2.5	15
2,4,6-triamino-s-triazinium 5,5′-azotetrazolate	2.2	13
TAGzT	4	18
Detonator (PETN RP-80)	2.2	18

and 2,4,6-triamino-s-triazinium 5,5′-azotetrazolate salt produced a dent depth of 2.2 mm and an internal blast peak quasi-static overpressure (P_{QS}) of 13 psig. These two test compounds produced dents about the same as the blank test (detonator alone), indicating that the compounds have little or no potential to detonate. Triaminoguanidinium 5,5′-azotetrazolate (TAGzT) was used as a standard that had a dent depth of 4.0 mm and an internal blast peak quasi-static overpressure (P_{QS}) of 18 psig. TAGzT does show shock reactivity and has a potential to detonate. Internal blast peak quasi-static overpressure (Pqs) generally correlates with total energy release. However, in the case of high-nitrogen propellants, their intrinsic lower flame temperatures combined with heat loss in a small-scale test may prevent efficient burning of combustible product species. The low internal blast pressures for the two test compounds compared to TAGzT suggest lower reactivity.

Experimental

CAUTION: *Although we experienced no difficulty handling these salts, care should be taken when handling these energetic materials.*

General Procedure

Sodium 5,5′-azotetrazole pentahydrate was prepared following the Thiele method [1]. It was added to a magnetically stirred

solution of the respective chloride in water. After 2 hr at room temperature, the solution was concentrated under vacuum to afford a solid.

5-Aminotetrazolium 5,5′-azotetrazolate ***(1)***. Yield 90%. DSC: $T_{Dec.} = 170°C$, $T_{Onset} = 134.3°C$ (274 J/g). IR (cm^{-1}): 3,580 (m), 1,650 (vs), 1,588 (vs), 1,400 (s), 1,265 (m), 1,195 (m), 1,192 (m), 1,148 (m), 1,071 (s), 1,050 (s), 779 (s), 739 (s), 733 (s), 680 (m). ^{1}H NMR (DMSO): δ 6.4, 3.2; ^{13}C NMR (DMSO): δ 174, 157. Density: 1.73 g/cm^3.

2,4,6-Triamino-s-triazinium 5,5′-azotetrazolate ***(2)***. Yield 90%. DSC: $T_{Dec.} = 270°C$, $T_{Onset} = 248.3°C$ (682 J/g). IR (cm^{-1}): 3,389 (m), 3,285 (m), 3,149 (m), 1,650 (vs), 1,662 (vs), 1,643 (vs), 1,606 (s), 1,559 (vs), 1,512 (m), 1,483 (m), 1,406 (m), 1,390 (m), 1,334 (m), 1,261 (m), 1,205 (m), 1,179 (m), 1,092 (m), 1,063 (m), 1,023 (m), 972 (m), 871 (m), 785 (m), 741 (m), 728 (m), 679 (m). ^{13}C NMR (DMSO): δ 163, 157. Density: 1.70 g/cm^3.

Conclusions

Salts of 5,5′-azotetrazolate dianion with 5-aminotetrazolate and 2,4,6-triamino-s-triazine cations were synthesized and studied. These salts showed good thermal stability and low to medium sensitivity to impact, friction, and electrostatic discharge. 5-Aminotetrazolium 5,5′-azotetrazolate had a dent depth of 2.5 mm, which was slightly more than an inert response, and 2,4,6-triamino-s-triazinium 5,5′-azotetrazolate had a dent depth of 2.2 mm, which was inert, producing a dent equivalent to the detonator.

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