

One-Pot Synthesis of Guanidinium 5,5'-Azotetrazolate Avoiding Isolation of Hazardous Sodium 5,5'-Azotetrazolate

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ABSTRACT: Sodium 5,5'-azotetrazolate (Na_2AzT) is a starting material for various azotetrazole salts that find applications as lead-free primary explosives or high-nitrogen compounds for inflating safety systems (in particular, guanidinium azotetrazolate, GZT). Sodium azotetrazolate, after preparation, is commonly isolated as the pentahydrate, which is relatively safe for handling. But it readily loses hydrate water molecules at higher temperatures or by treatment with organic solvents. In such cases, sensitivity to mechanical stimuli increases considerably and explosion accidents may occur. In this work, the thermal conditions and the role of solvents in water loss from sodium 5,5'-azotetrazolate pentahydrate are presented. Impact and friction sensitivity parameters of the products are described. In the case of guanidinium azotetrazolate, the process for its preparation without producing sodium 5,5'-azotetrazolate is introduced, thus avoiding manipulation of hazardous material and increasing the safety of the procedure.

KEYWORDS: sodium azotetrazolate, guanidinium azotetrazolate, improved synthesis, sensitivity to impact and friction

INTRODUCTION

Sodium 5,5'-azotetrazolate pentahydrate (Figure 1) is used as a starting material for producing various azotetrazole energetic

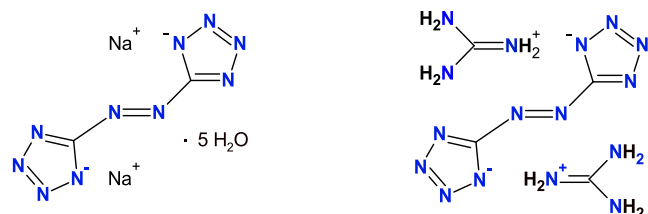


Figure 1. Structural formulas of sodium 5,5'-azotetrazolate pentahydrate ($\text{Na}_2\text{AzT}\cdot 5\text{H}_2\text{O}$) and guanidinium 5,5'-azotetrazolate (GZT).

salts and azo-compounds.^{1–5} Bismuth, copper, or silver salts of azotetrazole are primary explosives sensitive to mechanical stimuli rendering them suitable for pyrotechnic initiator compositions.^{6–8} These compositions are free of lead or nitrophenol salts, thus possessing lower toxicity that leads to a low environmental impact. Sodium 5,5'-azotetrazolate pentahydrate is proposed for use in gas generating pyrotechnic compositions used as airbags or fire extinguishing agents.^{9–12}

Many azotetrazolates with nitrogen-rich cations, in particular ammonium, guanidinium, and triaminoguanidinium azotetrazolates, find applications in the area of green energetic materials such as gas generators, ammunition propellants, and fireworks.³ Triaminoguanidinium azotetrazolate is highly effective, with its high nitrogen content and an elevated heat of formation. Therefore, it is suggested for nitrogen-rich propellants^{13,14} like Navy Insensitive Low-Erosion Propellant (NILE-propellant).¹⁵ The most suitable high-nitrogen azotetrazolate is guanidinium 5,5'-azotetrazolate (GZT, Figure 1) because of its superior chemical stability and its lack of

sensitivity to mechanical stimuli. For these reasons, GZT has a wide range of applications in gas generation for safety systems, such as airbags^{16–20} or safety belt pretensioners.²¹ Other uses of GZT are to be found in the following list: as an additive to fireworks,²² as a component in pyrotechnic infrared decoys,²³ as an additive to high-performance hybrid rocket fuels,²⁴ as a reduced-erosion additive to propellants,²⁵ in pyrotechnic mixtures used for deep drawing applications,²⁶ as a gas generator for fire extinguishing systems,^{27–29} or as a component of adhesive compositions in the semiconductor industry.³⁰

Guanidinium 5,5'-azotetrazolate (Figure 1) is prepared from sodium 5,5'-azotetrazolate and the guanidine salt.^{3,31} The intermediate, sodium 5,5'-azotetrazolate, was first prepared by Thielle in 1898 by the oxidation of 5-aminotetrazole with potassium permanganate in the presence of sodium hydroxide.¹ Although other methods have been published,^{32–34} various modifications of Thielle's¹ process remain the principal method for its synthesis.^{3,7,35–36}

Because of the easy transition of 5,5'-azotetrazolate pentahydrate to the more sensitive forms and the associated hazards, we have focused on the conditions for the transition of pentahydrate to lower hydrates and on their sensitivity to mechanical stimuli. In the case of the production of guanidinium 5,5'-azotetrazolate, where sodium 5,5'-azotetrazolate pentahydrate is an intermediate, we concentrated on

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developing a one-step production process without isolation of the potentially hazardous sodium salt.

RESULTS AND DISCUSSION

Impact and Friction Sensitivity of Sodium 5,5'-Azotetrazolate and Its Hydrates. Sodium 5,5'-azotetrazolate exhibits explosive properties and must be treated as a hazardous material. From the viewpoint of handling safety, it is important to know the sensitivity to mechanical stimuli, such as impact and friction. In the literature, there are uncertainties regarding the exact sensitivity data for sodium 5,5'-azotetrazolate hydrates, which are based on the existence of both its several hydrates and its anhydrous form. Some authors mention the high sensitivity of the 5,5'-azotetrazolate sodium salt, without additional information concerning the amount of hydrate water, or with the sensitivity being described in general terms, such as the hydrates being less sensitive or insensitive with the anhydrous salt being very sensitive.^{2,3,37–44}

Because a comprehensive evaluation and comparison of the sensitivity to mechanical stimuli of sodium azotetrazole and its hydrates are lacking, we have provided detailed sensitivity characteristics. The sensitivity of the substances examined is expressed as the dependence of the initiation probability on the impact energy and friction force.

Regarding the size and shape of the crystals of the measured substances, sodium azotetrazolates were in the form of rod and cubic-like crystals with the following major dimensions: pentahydrate 130–1100 μm , dihydrate 90–600 μm , and 120–800 μm for anhydrous 5,5'-sodium azotetrazolate. Guanidinium azotetrazolate was in the form of needles with major dimensions of 30–300 μm . Optical microscope images of the crystals are shown in Figure S1.

Since the sensitivity values measured in different laboratories may vary, comparison of the results with the sensitivities of long-term manufactured and well-examined explosives, like the primary explosive mercury fulminate (MF) and the highly explosive pentaerythritol tetranitrate (PETN), were carried out.

In the case of impact sensitivity, the pentahydrate of sodium 5,5'-azotetrazolate was found to be completely insensitive to this stimulus. In our case, we did not get any initiation from ten measurements using an impact energy of 100 J. The impact sensitivity of the dihydrate is half that of PETN, while the anhydrous salt is slightly more sensitive than PETN (Figure 2, 50% probabilities of initiation are summarized in Table 1).

In the case of friction sensitivity, sodium 5,5'-azotetrazolate pentahydrate was not found to be completely insensitive (as is sometimes reported in the literature²); in the case of the highest friction force of 360 N, 5 activations out of 15 trials were found. Sodium 5,5'-azotetrazolate pentahydrate is thus on the borderline of substances considered as explosives in terms of transportation hazards.⁴⁵ The sensitivity of the dihydrate is quite high and is close to that for pentaerythritol tetranitrate. Surprisingly, the anhydrous salt is very sensitive to friction, its sensitivity even exceeding that of mercury fulminate.^{44b} The sensitivity curves for both the dihydrate and anhydrous salt are shown in Figure 3, and the 50% initiation probability values are summarized in Table S1.

On the basis of these results, both the dihydrate and anhydrous sodium 5,5'-azotetrazolates are highly sensitive materials. Handling and storage of such substances are dangerous and pose the same risk as any other explosive.

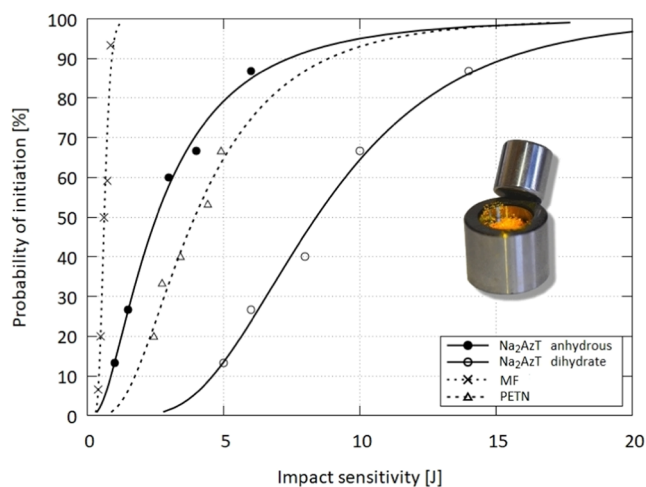


Figure 2. Impact sensitivity curves of anhydrous salt and dihydrate of sodium 5,5'-azotetrazolate compared with mercury fulminate (MF) and pentaerythritol tetranitrate (PETN).

Table 1. Friction and Impact Sensitivities and Parameters of Sensitivity Curves for Sodium 5,5'-Azotetrazolate, Mercury Fulminate, and Pentaerythritol Tetranitrate^a

sample	sensitivity to impact			sensitivity to friction		
	E_{50} [J]	μ	σ	F_{50} [N]	μ	σ
$\text{Na}_2\text{AzT} \cdot 2\text{H}_2\text{O}$	8.4	2.13	0.470	99	4.59	0.345
Na_2AzT anhydrous	2.5	0.930	0.835	1.2	0.157	0.517
MF	0.62	-0.477	0.291	5.4	1.68	0.610
PETN	3.9	1.37	0.633	75	4.32	0.298

^a E_{50} —impact energy at 50% initiation probability, F_{50} —friction force at 50% initiation probability, μ —mean (parameter of sensitivity curve), σ —standard deviation (parameter of sensitivity curve).

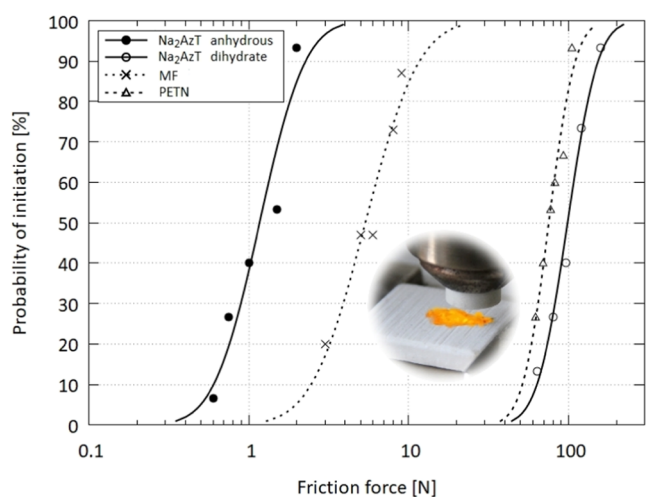


Figure 3. Friction sensitivity curves of anhydrous salt and dihydrate of sodium 5,5'-azotetrazolate compared with mercury fulminate (MF) and pentaerythritol tetranitrate (PETN).

On the other hand, guanidinium 5,5'-azotetrazolate (GZT) is completely insensitive to both impact and friction. We did not obtain any activation out of ten trials using an impact energy of 100 J and friction force of 360 N.

Sodium 5,5'-Azotetrazolate Hydrates and Their Changes. The conditions for the preparation and storage of sodium 5,5'-azotetrazolate determine the form in which it occurs. Because of the high sensitivity of sodium 5,5'-azotetrazolate dihydrate and anhydrous forms, we focused in detail on the effects that cause the loss of crystal waters. Key factors include temperature, air humidity, and the solvents used.

The effects of an elevated temperature on the loss of the crystal waters are evident from the differential thermal analysis (DTA) and thermogravimetric analysis (TG) thermograms (Figure 4). The DTA thermogram of sodium 5,5'-azotetrazo-

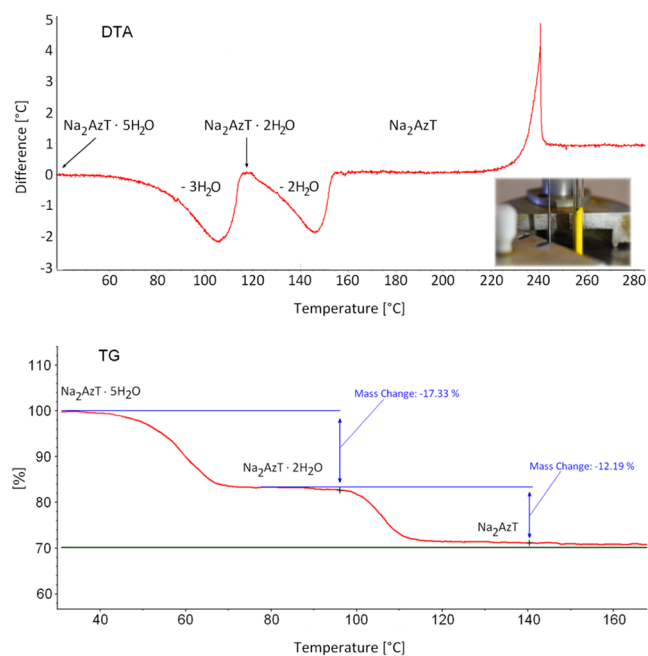


Figure 4. DTA and TG thermograms of sodium 5,5'-azotetrazolate pentahydrate indicate areas of appearance of various hydrates.

late pentahydrate shows that the formation of the dihydrate takes place at 55 °C, where three water molecules leave, with further dehydration occurring at 120 °C to form the anhydrous material. Decomposition occurs at 220 °C and is accompanied by explosion leading to damage of the DTA micro test tube in most cases. With prolonged thermal exposure, water loss can occur even at significantly lower temperatures (Table 2).

In addition to the temperature, humidity is also an important factor for crystal water losses. Weight changes at

various humidity levels show that sodium 5,5'-azotetrazolate pentahydrate is only slightly hygroscopic at 90% air humidity (Table 2). On the contrary, at 30% air humidity, the pentahydrate loses water at 30 °C, and after 10 days, it corresponds to sodium 5,5'-azotetrazolate dihydrate. Even at 50% humidity, pentahydrate loses a small, but measurable, amount of water. The dihydrate loses little water at 30% humidity, while, at 50 and 90% air humidity, the dihydrate absorbs water to form the pentahydrate. As expected, anhydrous sodium 5,5'-azotetrazolate takes up water from the air at all measured humidity levels. At 30% air humidity 30% the dihydrate is formed, and at both 50 and 90% air humidity, the pentahydrate appears. These data indicate that air humidity is an important factor for safe storage, especially at humidity levels of around 30% and lower.

Sodium 5,5'-azotetrazolate was prepared^{1,2} in an aqueous environment crystallizes as the pentahydrate. It is also soluble in several organic solvents (Table S1). However, recrystallization of pentahydrate from methanol or dimethylsulfoxide/acetone leads to the formation of the dihydrate.

Because of the risk of dehydration and forming of an explosive material, sodium 5,5'-azotetrazolate pentahydrate is wetted during transport to prevent possible loss of water.⁴⁵ The amount of wetting water is usually 25%. When processing the substance in industry, the wetting water is removed with a solvent miscible with water and which does not dissolve the required material. During our work, we recognized that several solvents remove not only wetted water, but they also remove some crystal water from the pentahydrate to form a pentahydrate/dihydrate mixture. (Table 3) This can result in two main difficulties: the material becomes sensitive to mechanical stimuli and unclear compositions may affect the intended stoichiometry of the subsequent reaction. Table 3 shows that water loss from the pentahydrate is dependent on the solvent used and the ratio of solvent to substance. Methanol removes hydrate water in all of the reaction conditions studied. In the case of dry ethanol, propanol, and acetone, only the dry pentahydrate is dehydrated. In the case of wetted sodium 5,5'-azotetrazolate pentahydrate, dehydration occurs only with excess alcohol being present. The small water content of ethanol prevents dehydration, and dehydration was not detected in any of the cases tested, which was also the case when using tetrahydrofuran. Of the solvents tested, we can recommend 96% ethanol as a cheap and readily available solvent.

Because the loss of crystal water from pentahydrate can easily take place, the state of sodium 5,5'-azotetrazolate during storage and handling should be checked. Infrared spectroscopy

Table 2. Weight Changes of 5,5'-Azotetrazolate and Its Hydrates at 30 °C at Various Air Humidity Levels

5,5'-azotetrazolate	air humidity (%)	weight changes (%)				
		1 day	3 days	10 days	30 days	60 days
pentahydrate	30	-5.19	-16.1	-17.9	-17.9	-17.9
	50	0.00	-0.15	-0.18	-0.20	-0.19
	90	0.34	0.50	0.51	0.50	0.50
dihydrate	30	-0.11	-0.15	-0.19	-0.25	-0.51
	50	0.16	2.55	14.5	21.2	21.2
	90	18.0	21.8	21.9	21.8	21.9
anhydrous	30	13.1	14.8	14.9	14.9	15.1
	50	26.5	35.3	42.1	42.3	42.2
	90	41.2	41.1	41.5	41.6	41.7

Table 3. Loss of Crystal Water of Dry and Wetted (25% Water) Sodium 5,5'-Azotetrazolate Pentahydrate during Interaction with Various Solvents, Expressed as Weight Ratio Sodium 5,5'-Azotetrazolate Pentahydrate/Solvent^{a,b}

solvent	sodium 5,5'-azotetrazolate pentahydrate/conditions			
	dry	wetted	wetted	wetted
	wt. ratio 4:1 4 h	wt. ratio 4:1 4 h	wt. ratio 4:1 4 days	wt. ratio 100:1 4 days
methanol	+	+	+	dissolved
ethanol, 100%	+	0	0	+
ethanol, 96%	0	0	0	0
propan-2-ol	+	0	0	+
propan-1-ol	+	0	0	+
acetone	+	0	0	+
tetrahydrofuran	0	0	0	0

^a+ Change to dihydrate or mixture of pentahydrate and dihydrate. ^b0 No interaction.

is a fast and simple method for identifying the hydrate forms of sodium 5,5'-azotetrazolate. The pentahydrate has four strong bands, while the dihydrate has just one band in the region of 4000–2800 cm⁻¹. Another area where there is a difference between hydrates is in the band of 1700–1500 cm⁻¹ (Figure 5).

Apart from infrared spectroscopy, it is possible to recognize the hydrates by Karl Fischer titration and differential thermal analysis or thermogravimetry (Figure 4), where a two-step loss of crystal water is evident.

Preparation of Guanidinium 5,5'-Azotetrazolate without Isolation of Sodium 5,5'-Azotetrazolate. Guanidinium 5,5'-azotetrazolate used as a gas generator is

commonly prepared from sodium 5,5'-azotetrazolate and a suitable guanidinium salt.³ Since the use of the sodium 5,5'-azotetrazolate pentahydrate is accompanied by difficulties associated with its water crystal changes (described above), which negatively affect handling safety, we have developed a convenient one-pot synthesis of guanidinium azotetrazolate without the need to isolate sodium 5,5'-azotetrazolate pentahydrate (Figure 6).

The first step—preparation of sodium 5,5'-azotetrazolate—is based on the published process.¹ In the original processes, the product is precipitated from the solution by evaporation of water³ or addition of ethanol.⁷ In our procedure, sodium 5,5'-azotetrazolate remains dissolved in the warm reaction mixture, guanidine hydrochloride is then added, and guanidinium 5,5'-azotetrazolate immediately precipitates. Because sodium hydroxide is present in excess in the reaction mixture, some of the guanidinium chloride can react with it, resulting in a relatively low yield of 66% at the stoichiometric amount of guanidinium chloride (Table 4). High yields above 75% can be achieved when guanidinium chloride is three times in excess of the stoichiometric value.

From an economic point of view, a variation may be interesting where, by neutralizing the sodium hydroxide in the reaction mixture with acetic acid, the amount of guanidinium chloride can be reduced to one-third. The yield in this arrangement is 71%.

The 78% yield slightly exceeds the highest yield (76%) reported in the literature (for the two-step process including separation of sodium 5,5'-azotetrazolate).^{3,46} Thus, dangerous Na₂AzT is not isolated and the process gives a high yield of GZT.

In addition, guanidinium 5,5'-azotetrazolate can be used as a starting material for other azotetrazolate salts. We have

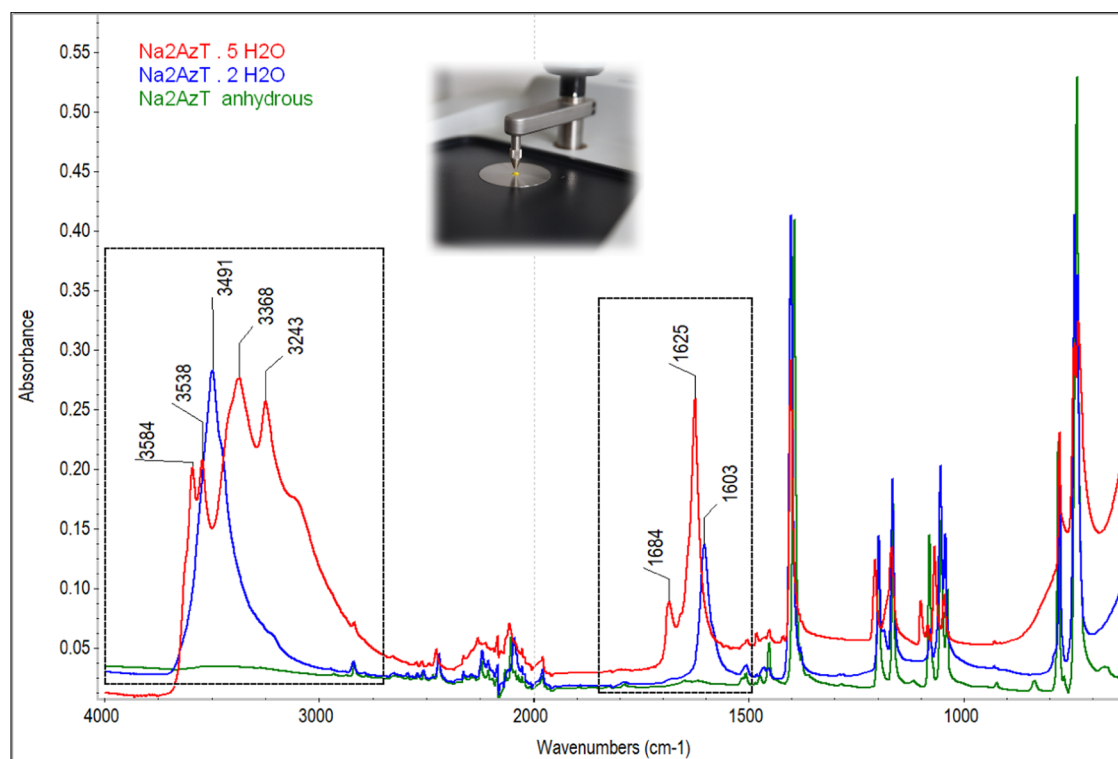


Figure 5. Infrared spectra of sodium 5,5'-azotetrazolate and its hydrates.

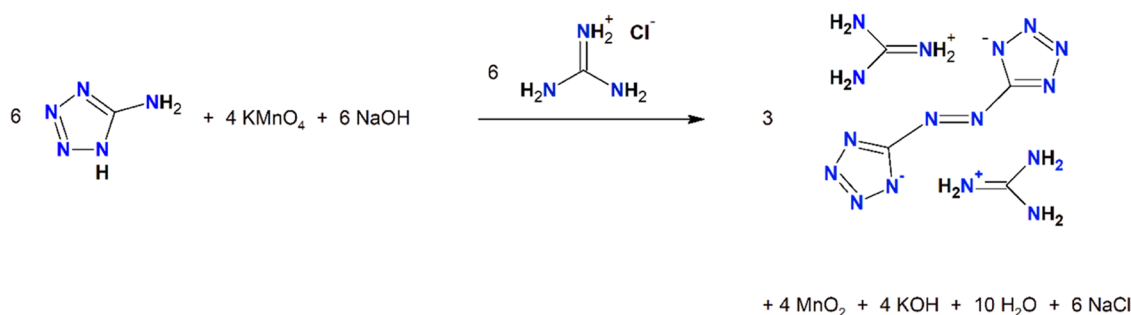


Figure 6. One-pot synthesis of guanidinium 5,5'-azotetrazolate without the isolation of sodium 5,5'-azotetrazolate.

Table 4. Yields of Guanidinium 5,5'-Azotetrazolate under Various Conditions

Gu-HCl/5-ATZ/AcOH molar ratio	3:1:0	2:1:0	1:1:0	1:1:1	1:1:2
GZT yield (%)	78	72	66	71	71

successfully verified this for the zinc and silver salts of 5,5'-azotetrazolate.

CONCLUSIONS

Sodium 5,5'-azotetrazolate pentahydrate is easily changed to the moderately sensitive dihydrate or to the highly sensitive anhydrous salt. These changes can be caused by increased temperature, even at common temperatures at low air humidity, or by the action of organic solvents.

For these reasons, the state of sodium 5,5'-azotetrazolate during storage and handling should be regularly monitored, with any changes connected with crystal waters being recognized by infrared spectroscopy, thermal analysis methods, or the Karl Fischer method.

For these reasons, it is better to avoid the sodium salt altogether and to use the handling-safe GZT as a starting material for other 5,5'-azotetrazole salts.

It is possible to prepare guanidinium 5,5'-azotetrazolate in a one-pot process from 5-aminotetrazole and guanidinium chloride. The synthesis is fast and safe, and the yield is even higher than the conventional two-step process via the sodium salt.

EXPERIMENTAL SECTION

General Methods. Solvents and reagents obtained from commercial sources were used without further purification. The thermal analysis was performed using a DTA 550Ex differential thermal analyzer (OZM Research, Czech Republic). The samples were tested in open glass micro test tubes in contact with air at a heating rate of 5 °C min⁻¹. The sample weights were 10 mg. The melting points were measured on a Kofler bench and are uncorrected. Elemental analysis was carried out using a UNICUBE (Elementar, Germany) automatic elemental analyzer on 1–2 mg samples. The infrared spectra were collected by using a Nicolet iS50 FTIR spectrometer (Thermo) with an attenuated total reflectance (ATR) single reflection diamond accessory GladiATR (PIKE). Measurement parameters were: spectral region 4000–400 cm⁻¹, resolution 4 cm⁻¹ and 64 scans. Spectral work was done using Omnic 9.2 software. The Raman spectra were measured using a Nicolet iS50 Raman module with the following settings: 1064 nm excitation laser at 100–500 mW power range, spectral region 4000–100 cm⁻¹, resolution 4 cm⁻¹ and 128 scans. Abbreviations related to infrared and Raman

spectra: s, strong; m, medium; w, weak; sh, shoulder; br, broad; ν , stretching vibration; δ , deformation vibration, asym., asymmetric, sym., symmetric. Band assignment was provided with the help of Socrates and spectral calculations. The density functional theory (DFT) calculations were performed using the B3LYP functional method along with the def-TZVPP basis set using the TURBOMOLE 7.1 software package^{47–49} together with TmoleX 4.2⁵⁰ as a graphical user interface. For vibrational analysis, the molecular structures of the compounds in the ground state were optimized using constructed molecular geometry according to crystallographic data (CCD 154867 for guanidinium azotetrazolate and CCDC 235627 for sodium azotetrazolate) obtained from the Cambridge Crystallographic Database (CCDC, Cambridge, U.K.). Densities of solid materials were determined using a helium pycnometer Accu Pyc II 1340 (MJ Micromeritics) at a temperature of 23.6 °C. The solubility of sodium 5,5'-azotetrazolate pentahydrate in water and organic solvents was estimated by the procedure where sodium 5,5'-azotetrazolate pentahydrate was added to solvent in a sufficient amount to make a suspension. The solvent was then gradually added to the point when dissolution occurred. The hygroscopicity of sodium 5,5'-azotetrazolate and its hydrates was determined by weighing samples at an appropriate air humidity level.⁵¹ The humidity levels of 90 and 50% were obtained using sulfuric acid solutions, while a 30% humidity level was obtained using silica gel. The amount of water in the various sodium 5,5'-azotetrazolate hydrates was determined using the Karl Fischer method with an 870 KF Titrino plus (Methrom, Swiss) using Hydranal Composite 5 agent (Honeywell). Sensitivity to impact was measured using a Kast fall hammer. The measurement apparatus and related supplies were manufactured by the aforementioned company, OZM Research (Hrochův Týnec, Czech Republic). We used a 1 kg hammer for the anhydrous salt of sodium 5,5'-azotetrazolate, a 2 kg hammer for the dihydrate of sodium 5,5'-azotetrazolate, and a 10 kg hammer for the pentahydrate of sodium 5,5'-azotetrazolate and GZT. Testing sets comprised steel guide rings BFH-SR and steel cylinders BFH-SC. The probit analysis was used for measuring and evaluation.⁵² Five energy levels were measured for 15 trials for each energy level. Sensitivity curves for the reference explosives mercury fulminate (MF) and pentaerythritol tetranitrate (PETN) were taken from our previous work.⁵³ Sensitivity to friction was determined using a BAM apparatus type FSA-12. Testing sets comprised porcelain BFST Pt 100 25 × 25 mm plates and porcelain BFST Pn 200 pegs. The measurement apparatus and related supplies were manufactured by OZM Research (Hrochův Týnec, Czech Republic). Probit analysis was used for measuring and evaluation.⁵² Five energy levels were

measured for 15 trials for each energy level. Sensitivity curves for reference explosives were taken from our previous work.⁵² A Zeiss Axio Scope.A1 microscope with an Axiocam 208 color camera and ZEN core 3.1 software were used for crystal imaging.

Syntheses. Caution: The compounds involved are explosive and potentially sensitive to mechanical and thermal stimuli such as friction, impact, heat, and electric spark. Safety equipment, such as goggles or a face shield, gloves, and ear protection, is strongly recommended. Metal salts of 5,5'-azotetrazolate should be stored in a conductive rubber cup.

Preparation of Sodium 5,5'-Azotetrazolate Pentahydrate. A modified procedure based on the literature^{1,2} was used. Potassium permanganate (23.5 g, 0.15 mol) was added to a solution of 5-aminotetrazole (17.0 g, 0.2 mol) and sodium hydroxide (11.0 g, 0.3 mol) in 100 mL of water at 65 °C at such a rate that the reaction mixture temperature was maintained between 80 and 90 °C. After the addition of potassium permanganate, the mixture was stirred at 80 °C for 10 min. A strip of filter paper was placed in the reaction mixture. Yellow color indicates that all potassium permanganate has reacted with the manganese dioxide. Green color means that the reaction mixture still contains unreacted potassium permanganate (K₂MnO₄). In this case, a few milliliters of a 10% aqueous solution of sodium thiosulfate pentahydrate was added to consume any remaining potassium permanganate. The reaction mixture was hot-filtered, and the filter cake was washed with 2 × 50 mL of hot water. The transparent orange filtrate was allowed to cool below 10 °C, and the precipitated sodium 5,5'-azotetrazolate pentahydrate was filtered and washed with a small amount of cold water to yield 19.8 g (66.1%) of sodium 5,5'-azotetrazolate pentahydrate in the form of yellow needle crystals. The raw product was recrystallized from water, mp 273–275 °C. Anal. Calcd for C₂H₁₀N₁₀Na₂O₅ (%): C 8.00, H 3.36, N 46.67. Found: C 8.00, H 3.33, N 46.21. Water by Karl Fischer (%): Calcd 30.0. Found 29.2. DTA: endotherm 1: 55 °C (start), 81 °C (onset), 106 °C (minimum); endotherm 2: 122 °C (onset), 146 °C (minimum); exotherm: 212 °C (start), 239 °C (maximum). Density: 1.67 g·cm⁻³ (lit.³⁴ 1.696 g·cm⁻³). FTIR (cm⁻¹): 3584m (ν OH), 3538m (ν OH), 3368s (ν OH), 3243s (ν OH), 3100sh, 2832w, 2447w, 2107w, 1684m (δ OH), 1625s (δ OH), 1480w (ν N=N azo), 1452w (ν C–N_{azo}), 1400s (in phase ν C–N_{tetrazol}), 1204m (tetrazole ring), 1165m (tetrazole ring), 1097w, 1065m (tetrazole ring-influence by crystal water by comparison with the dihydrate and anhydrous Na₂AzT), 1044w, 926vw, 774m (δ CN₃ in tetrazole), 739s and 730s (ν CN_{azo} plus δ CNN tetrazole), 559sh, 508m. Raman (cm⁻¹): 1483s (ν N=N azo), 1421m (ν C–N_{tetrazol}), 1388s (in phase ν CN azo and ν C'N' azo), 1362w, 1204w, 1167w (in phase ν tetrazole rings, influenced by crystal water), 1099m, 1080w, 1067m (tetrazole ring), 926m (sym. CN₃ in azotetrazole), 333w.

Preparation of Sodium 5,5'-Azotetrazolate Dihydrate. *Method A: Crystallization from Dimethylsulfoxide/Acetone.* Sodium 5,5'-azotetrazolate pentahydrate (0.47 g, 1.9 mmol) was dissolved in 5 mL of dimethylsulfoxide and stirred for 15 min. Acetone (15 mL) was added, and the mixture was stirred for an additional 30 min. The precipitated yellow solid was filtered and washed with acetone to yield 0.25 g (65% yield) of the yellow solid. Mp 273–276 °C. DTA, endotherm: 124 °C (onset), 147 °C (minimum); exotherm: 208 °C (start), 246 °C (maximum). Anal. Calcd for C₂H₄N₁₀ Na₂O₂

(%): C 9.76, H 1.64, N 56.92. Found: C 9.83, H 1.68, N 56.37. FTIR (cm⁻¹): 3491s (ν OH), 3455sh (ν OH), 3025w, 2835w, 2436w, 2086w, 1603m (δ OH), 1480w (ν N=N azo), 1400s (in phase ν C–N_{tetrazol}), 1195m (tetrazole ring), 1163m (tetrazole ring), 1076w, 1051m 1050 (tetrazole ring), 1041m, 773m (δ CN₃ in tetrazole), 738s and 732s (ν CN_{azo} plus δ CNN tetrazole), 577sh (δ CN_{azo}), 461s, 425s. Raman (cm⁻¹): 1491s (ν N=N azo), 1426m (ν C–N_{tetrazol}), 1389s (in phase ν CN azo and ν C'N' azo), 1363w, 1194w, 1164w (in phase ν tetrazole rings), 1081m, 1057m (tetrazole ring), 931m (sym. CN₃ in azotetrazole), 337w.

Method B: Thermal Dehydration. Sodium azotetrazole pentahydrate (0.50 g, 1.7 mmol) in an aluminum pan was placed on a hot surface at a temperature of 60 °C for 80 min to yield 0.41 g (100%) of sodium azotetrazole dihydrate. Mp 274–276 °C. DTA, endotherm: 122 °C (onset), 147 °C (minimum), exotherm: 206 °C (start), 238 °C (maximum). Anal. Calcd for C₂H₄N₁₀Na₂O₂ (%): C 9.76, H 1.64, N 56.92. Found: C 9.72, H 1.64, N 56.93. Water by Karl Fischer (%): Calcd 14.6. Found 13.7. Density: 1.86 g·cm⁻³. Spectral characteristics are the same as the product prepared by method A. Small quantities of up to 200 mg can be obtained on the DTA apparatus, after stopping the heating of the pentahydrate sample at 100 °C, when the first endotherm ends.

Preparation of Anhydrous Sodium Azotetrazolate. Sodium 5,5'-azotetrazolate pentahydrate (0.50 g, 1.7 mmol) in an aluminum pan was placed in a dryer and dried at 125–135 °C for 2 h to give 0.35 g of sodium 5,5'-azotetrazolate (100%), mp 275–277 °C. Anal. Calcd for C₂N₁₀Na₂ (%): C 11.44, H 0.00, N 66.68. Found: C 11.46, H 0.23, N 65.61. DTA, exotherm: 192 °C (start), 235 °C (maximum). Density: 1.91 g·cm⁻³. Small samples of up to 200 mg may be prepared in a micro test tube using DTA apparatus, stopped at 165 °C (after the endotherm finish). FTIR (cm⁻¹): 2831w, 2437w, 2237vw, 2100w, 1505vw, 1484 (ν N=N azo), 1472w, 1452m, 1393s (in phase C–N tetrazol), 1375w, 1195m (tetrazole ring), 1161m (tetrazole ring), 1077m, 1050m (tetrazole ring), 776m (δ CN₃ in tetrazole), 733s (ν CN_{azo} plus δ CNN tetrazole), 563m (δ CN_{azo}), 450m. Raman (cm⁻¹): 1481s (sym N=N str), 1420m (ν C–N tetrazol), 1386s (in phase ν CN azo and ν C'N' azo), 1359w, 1161w (in phase ν tetrazole rings), 1088m, 1058m (tetrazole ring) 1050, 926m (sym. CN₃ in azotetrazole), 740w, 383m.

Preparation of Guanidinium 5,5'-Azotetrazolate. In a 5 L sulfonation flask, sodium hydroxide (88 g, 2.2 mol) and 5-aminotetrazole (136 g, 1.6 mol) were dissolved in 0.8 L of water. The reaction mixture was heated to 65 °C and potassium permanganate (188 g, 1.19 mol) was added in small portions to keep the temperature between 80 and 90 °C. Sodium thiosulfate pentahydrate (8 g, 0.03 mol) in 20 mL of water was added to the reaction mixture, and the mixture was hot-filtered and washed with 0.8 l water. The clear filtrate was poured into a 2 L glass laboratory reactor, heated to 70 °C, glacial acetic acid (74.5 g 1.188 mol) was added, and stirred for 10 min. A solution of guanidine hydrochloride (152.9 g 1.6 mol) in 100 mL of water was added dropwise using a separating funnel, and the reaction mixture was stirred at 70 °C for 2 h, then cooled to 9 °C and filtered, and washed with 480 mL of cold water and finally with 160 mL of ethanol to yield 161.3 g (71% calculated to 5-aminotetrazol), mp 253–255 °C. DTA, exotherm: 230 °C (start), 245 °C (maximum). Anal. Calcd for C₄H₁₂N₁₆ (%): C 16.90, H 4.22, N 78.87. Found: C 16.85, H 4.03, N 75.59. Density: 1.55 g·cm⁻³ (lit.³ 1.538 g

cm^{-3}). FTIR (cm^{-1}): 3442s (ν NH_2), 3393s (ν NH_2), 3198s (ν NH_2), 3093s (ν NH_2), 1697m (δ NH_2), 1652s (δ NH_2), 1586m, 1571m (δ NH_2 plus in plane ν CN in guanidine), 1399m (in phase ν $\text{CN}_{\text{tetrazol}}$), 1197m (tetrazole ring plus rock NH_2), 1176m, 1161 (tetrazole ring), 1082w, 1050m (tetrazole ring), 768m, 737s (ν CN_{azo} plus δ CNN tetrazole), 572m (δ CN_{azo}) plus rock (NH_2), 533m (δ CN in guanidine). Raman (cm^{-1}): 1482s (ν $\text{N}=\text{N}$ azo), 1442m (ν $\text{CN}_{\text{tetrazole}}$), 1385s (in phase ν CN azo and ν C'N' azo), 1087m, 1057s (tetrazole ring), 1010m (sym ν CN_3 in guanidine), 927m (sym ν CN_3 in azotetrazole), 544w, 531w, 339w.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.oprd.4c00364>.

Optical microscope images of 5,5'-azotetrazolates studied (Figure S1) and solubility data for sodium 5,5'-azotetrazolate pentahydrate (Table S1) (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. M.L. scaled-up synthesis, evaluated results, and drafted the manuscript. Z.J. organized the work, suggested the synthesis, measured density, and measured and evaluated infrared spectra. R.M. provides and evaluates sensitivity parameters. J.M. calculated and evaluated infrared and Raman spectra. A.V. provided syntheses and optimization of procedures.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

5-ATZ, 5-aminotetrazole; DTA, differential thermal analysis; FTIR, Fourier transform infrared spectroscopy; Gu-HCl, guanidinium hydrochloride; GZT, guanidium 5,5'-azotetrazolate; MF, mercury fulminate; mp, melting point; Na_2AzT , sodium 5,5'-azotetrazolate; PETN, pentaerythritol tetranitrate

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