

Article

# Structures and Energetic Properties of Two New Salts Comprising the 5,5'-Azotetrazolate Dianion

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† Dedicated to Professor Reinhard Kramolowsky on the occasion of his 80th birthday.

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**Abstract:** Two new potentially energetic salts comprising the 5,5'-azotetrazolate dianion have been prepared and structurally characterized. The new azotetrazolates are tetraphenylphosphonium-5,5'-azotetrazolate (**1**) and 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (**2**). The crystal structures of both compounds have been determined by single-crystal X-ray diffraction and their energetic properties have been tested. Due to its high nitrogen-content of 73.14%, compound **2** was found to be significantly impact-sensitive.

**Keywords:** energetic salts; azotetrazolate; phosphonium; 1*H*-1,2,4-triazole-1-carboxamidine; hydrogen bonds

## 1. Introduction

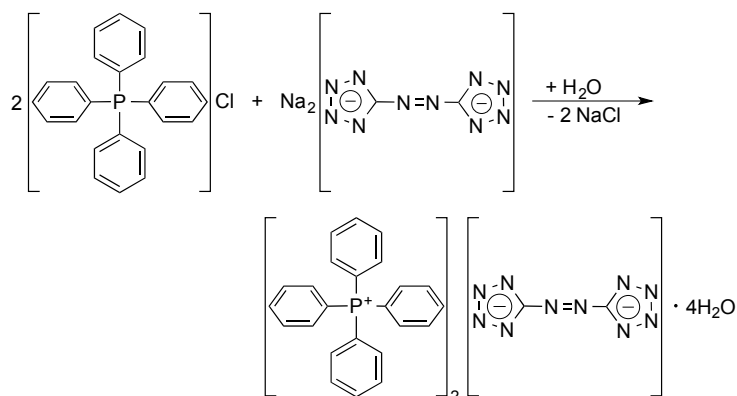
Nitrogen-rich energetic salts form an important class of explosive compounds. Several significant advantages such as high heats of combustion, high propulsive power, high specific impulse, as well as smokeless combustion make them highly useful as propellants, explosives, and pyrotechnics [1–6]. Among the most widely used nitrogen-rich anions is the 5,5'-azotetrazolate dianion,  $C_2N_{10}^{2-}$ , which was first reported by Thiele as early as 1898 [7]. The structural chemistry of 5,5'-azotetrazolate with various metals [8–18] as well as nitrogen- or phosphorus-containing cations [19–33] has been thoroughly investigated. We report here the synthesis and structural characterization of two new azotetrazolate salts,

tetraphenylphosphonium-5,5'-azotetrazolate (**1**) and 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (**2**).

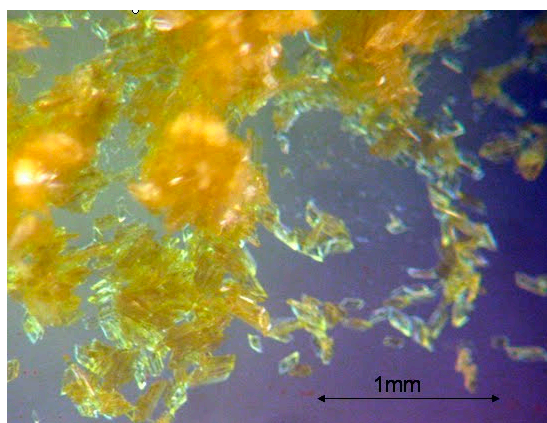
## 2. Results and Discussion

### 2.1. Synthesis and Characterization of Tetraphenylphosphonium-5,5'-azotetrazolate (**1**)

The starting material, hydrated disodium-5,5'-azotetrazolate,  $\text{Na}_2\text{C}_2\text{N}_{10}\cdot 5\text{H}_2\text{O}$ , was prepared according to the original protocol described by Thiele by oxidation of 1-aminotetrazole with  $\text{KMnO}_4$  in boiling sodium hydroxide solution [7]. A salt metathesis reaction of  $\text{Na}_2\text{C}_2\text{N}_{10}\cdot 5\text{H}_2\text{O}$  with 2 equiv. of tetraphenylphosphonium chloride in water according to Scheme 1 afforded tetraphenylphosphonium-5,5'-azotetrazolate,  $[\text{PPh}_4][\text{C}_2\text{N}_{10}]\cdot 4\text{H}_2\text{O}$  (**1**), in 78% isolated yield. The reaction initially produced an amorphous yellow precipitate, which was isolated by filtration and dried in air. Recrystallization from a minimum amount of reagent grade acetone afforded yellow, prism-shaped single-crystals which were found to be suitable for X-ray diffraction (Figure 1).



**Scheme 1.** Preparation of tetraphenylphosphonium-5,5'-azotetrazolate (**1**).

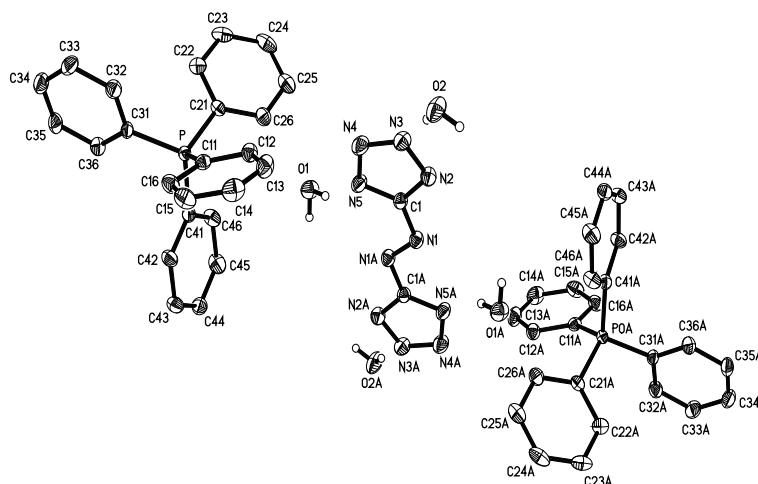


**Figure 1.** Crystals of tetraphenylphosphonium-5,5'-azotetrazolate (**1**).

Tetraphenylphosphonium-5,5'-azotetrazolate (**1**) was fully characterized through IR and NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) spectroscopy as well as single-crystal X-ray diffraction. Both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were in good agreement with the expected structure. For example, the  $^1\text{H}$  NMR spectrum showed a multiplet at  $\delta$  7.95 ppm for the phenyl hydrogens in *para*-position and a broad multiplet at  $\delta$  7.83–7.67 ppm

attributable to the *ortho*- and *meta*-phenyl protons. The  $^{31}\text{P}$  NMR spectrum showed a single resonance at  $\delta$  23 ppm. In the IR spectrum, a strong band at  $1374\text{ cm}^{-1}$  can be assigned to the asymmetric N–C=N stretching vibration of the tetrazole ring, while a strong band at  $724\text{ cm}^{-1}$  is characteristic for the asymmetric C–N=N stretching vibration of the azotetrazolate dianion [19–33].

A single-crystal X-ray diffraction study of **1** revealed that the compound crystallizes as the tetrahydrate  $[\text{PPh}_4]_2[\text{C}_2\text{N}_{10}]\cdot 4\text{H}_2\text{O}$  in the triclinic space group  $\text{P}\bar{1}$ . Figure 2 shows the molecular structure of **1** along with selected bond lengths and angles. Table 1 lists the crystallographic data and structure refinement details for the title compounds.



**Figure 2.** Molecular structure of **1** in the crystal, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–N(1A) 1.256(4), N(2)–N(3) 1.338(3), N(3)–N(4) 1.326(3), N(4)–N(5) 1.347(3), C(1)–N(1) 1.404(3), C(1)–N(2) 1.335(3), C(1)–N(5) 1.332(3); C(11)–P–C(4) 108.14(11), C(21)–P–C(41) 109.13(12), C(31)–P–C(21) 108.10(12), C(31)–P–C(11) 107.82(11), C(21)–P–C(11) 112.47(11), C(31)–P–C(41) 111.20(11) (#1  $-x + 1, -y, -z$ ).

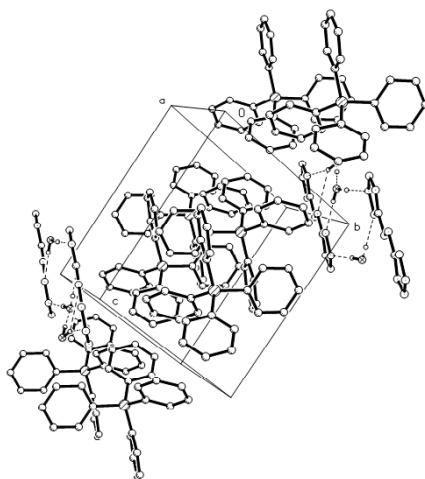
**Table 1.** Crystallographic data and structure refinement details for compounds **1** and **2**.

Compound	1	2
CCDC No.	1404740	1404741
Empirical formula	$\text{C}_{25}\text{H}_{24}\text{N}_5\text{O}_2\text{P}$	$\text{C}_8\text{H}_{12}\text{N}_{20}$
<i>a</i> (Å)	10.159(2)	11.6127(2)
<i>b</i> (Å)	10.632(2)	9.95120(10)
<i>c</i> (Å)	11.632(2)	6.81850(10)
$\alpha$ (°)	80.34(3)	90
$\beta$ (°)	80.22(3)	103.383(2)
$\gamma$ (°)	72.85(3)	90
<i>V</i> (Å <sup>3</sup> )	1173.9(4)	766.551(19)
<i>Z</i>	2	2
Formula weight	457.46	388.38
Space group	$\text{P}\bar{1}$	$\text{P}2_1/\text{c}$
<i>T</i> (°C)	−140	−173
$\lambda$ (Å)	0.71073	0.71073

Table 1. Cont.

Compound	1	2
Crystal size (mm <sup>3</sup> )	0.29 × 0.18 × 0.15	0.35 × 0.27 × 0.25
Crystal colour/shape	yellow/prism	yellow/prism
Reflections collected	14492	32565
Independent reflections	6289	1889
<i>R</i> (int)	0.0736	0.0329
<i>D</i> <sub>calcd</sub> (g·cm <sup>−3</sup> )	1.294	1.683
<i>μ</i> (mm <sup>−1</sup> )	0.149	0.128
<i>F</i> (000)	480	400
data/restraints/parameters	6289/0/314	1889/0/151
goodness-of-fit on <i>F</i> <sup>2</sup>	1.126	1.086
Final <i>R</i> 1 index [ <i>I</i> > 2σ( <i>I</i> )]	0.0735	0.0326
Final <i>R</i> 2 index [ <i>I</i> > 2σ( <i>I</i> )]	0.1160	0.0772
<i>R</i> 1 index (all data)	0.1146	0.0376
<i>R</i> 2 index (all data)	0.1267	0.0796
Largest diff. peak/hole (e. Å <sup>−3</sup> )	0.447/−0.306	0.274/−0.268

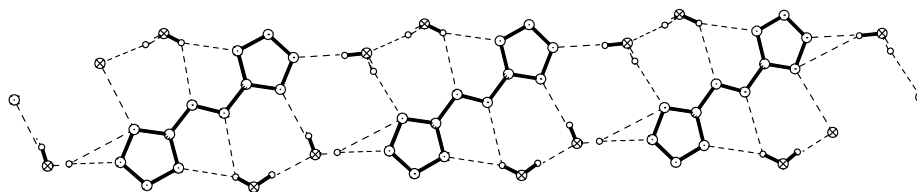
All structural parameters in the cations and anions in **1** are unexceptional and in close agreement with those of previously reported azotetrazolates. The central N=N distance in the azotetrazolate dianion is 1.256(4) Å, while the N–N bond lengths in the tetrazole rings fall in the narrow range of 1.326(3)–1.347 Å. The tetraphenylphosphonium cations in **1** show only minor deviations from the ideal tetrahedral geometry. C–P–C angles are all in the range of 107.82(11)–112.47(11)°, while the aromatic C–C bond lengths are between 1.378 and 1.402 Å. A comparable range of the C–P–C angles (107.9–110.4°) has been reported for the recently described bis(tetramethylphosphonium)-5,5'-azotetrazolate, [PMe<sub>4</sub>]<sub>2</sub>[C<sub>2</sub>N<sub>10</sub>] [33]. Like virtually all previously reported azotetrazolate salts [19–33], the crystal structure of **1** is characterized by an array of hydrogen bonds. Figure 3 shows the unit cell of compound **1**.



**Figure 3.** Packing diagram of tetraphenylphosphonium-5,5'-azotetrazolate (**1**). Dashed lines represent hydrogen bonds.

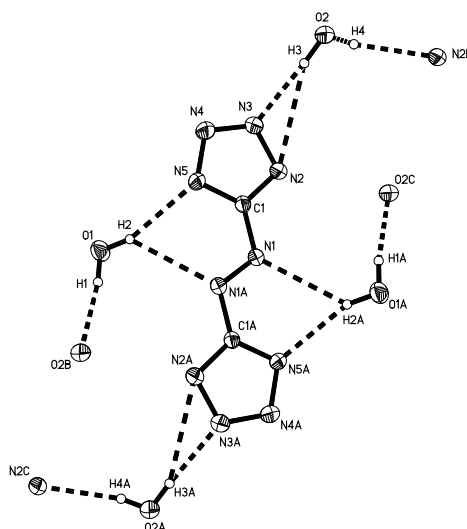
The packing diagram of **1** (Figure 3) shows that hydrogen bonding is an important factor in stabilizing the solid-state structure. However, in contrast to the [PMe<sub>4</sub>]<sup>+</sup> cations in the recently reported crystal

structure of bis(tetramethylphosphonium)-5,5'-azotetrazolate [33], the phenyl rings of the  $[\text{PPh}_4]^+$  cations in **1** do not participate in the hydrogen bonding. The reason for this structural difference can be seen in the fact that **1** crystallizes as the tetrahydrate  $[\text{PPh}_4]_2[\text{C}_2\text{N}_{10}] \cdot 4\text{H}_2\text{O}$ , whereas  $[\text{PMe}_4]_2[\text{C}_2\text{N}_{10}]$  was isolated as an anhydrous material [33]. As can be seen in Figure 4, the 5,5'-azotetrazolate dianions are interconnected through hydrogen bonds with the four molecules water of crystallization to give a ladder-like ribbon motif.



**Figure 4.** Ribbon motif formed through hydrogen bonding between the 5,5'-azotetrazolate dianions and the water of crystallization in the crystal structure of **1**.

Figure 5 illustrates in more detail how three tetrazole ring nitrogen atoms as well as the N atoms of central azo group are engaged in the O–H...N hydrogen bonds to the four water molecules. O–H...O hydrogen bonds between two water molecules are also present on both sides of the ribbon. Details of the hydrogen bonding in the solid-state structure of **1** are summarized in Table 2.



**Figure 5.** Hydrogen bonding between the 5,5'-azotetrazolate dianions and the water of crystallization in the crystal structure of **1**.

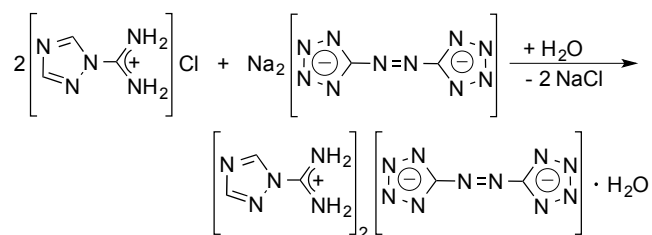
**Table 2.** Hydrogen bond lengths [Å] in **1**.

D–H...A	d(D–H)	d(H...A)	d(D...A)
O(1)–H(1)...O(2)#2	0.87 (4)	1.95 (4)	2.811 (3)
O(1)–H(2)...N(5)	0.87 (4)	2.28 (4)	3.115 (3)
O(1)–H(2)...N(1)#1	0.87 (4)	2.62 (4)	3.274 (3)
O(2)–H(3)...N(3)	0.88 (4)	2.05 (4)	2.925 (3)
O(2)–H(4)...N(2)#3	0.79 (4)	2.14 (4)	2.913 (3)

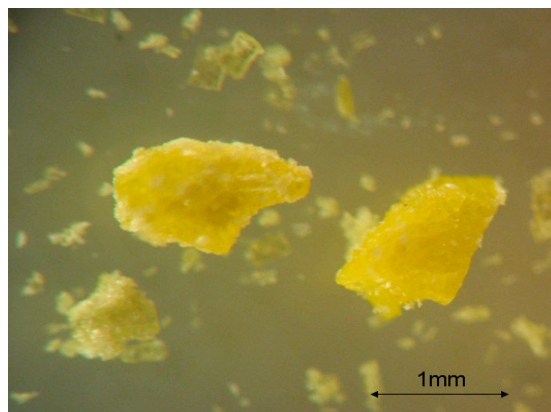
#1  $-x + 1, -y, -z$ ; #2  $x + 1, y, z$ ; #3  $-x, -y, -z$ .

## 2.2. Synthesis and Characterization of 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (2)

A second potentially energetic azotetrazolate salt prepared and characterized in the course of this work is the hitherto unknown 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (**2**) which was made according to Scheme 2 by treatment of Na<sub>2</sub>C<sub>2</sub>N<sub>10</sub>·5H<sub>2</sub>O with 2 equiv. of 1*H*-1,2,4-triazole-1-carboxamidine-hydrochloride. After short reaction times, bright yellow crystals of **2** (Figure 6) formed in 86% isolated yield.



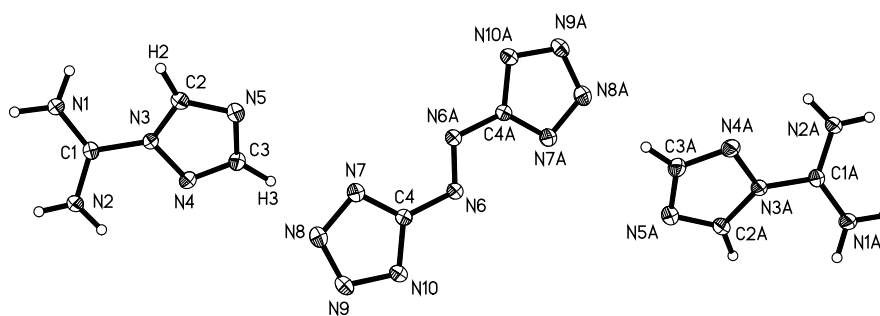
**Scheme 2.** Preparation of 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (**2**).



**Figure 6.** Crystals of 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (**2**).

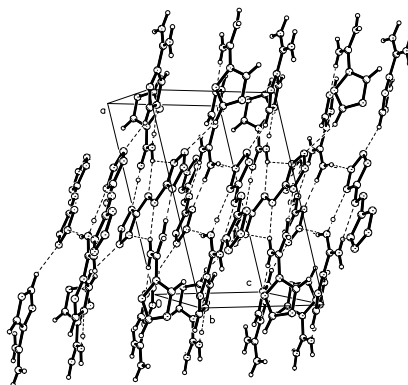
Both the ease of formation and the high isolated yield of **2** indicated that the 1*H*-1,2,4-triazole-1-carboxamidine cation is a valuable tool for isolating energetic anion species. The <sup>1</sup>H NMR spectrum of **2** displayed only two singlets at 2.49 and 8.29 ppm, which could be assigned to the amidinium C(NH<sub>2</sub>)<sub>2</sub> protons and the triazole ring NH protons, respectively. In good agreement with the expected formation of **2**, the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum showed only three resonances at δ 153.2 (CN<sub>4</sub> of azotetrazolate), 149.8 (C=N of triazole ring), and 144.5 (C(NH<sub>2</sub>)<sub>2</sub>) ppm. In the IR spectrum, a strong band at 1393 cm<sup>−1</sup> was assigned to the asymmetric N–C=N stretching vibration of the tetrazole ring, whereas a strong band at 723 cm<sup>−1</sup> was due to the asymmetric C–N=N stretching vibration of the azotetrazolate dianion [19–33]. Bands in the range of 3127 cm<sup>−1</sup> to 2329 cm<sup>−1</sup> are typical for the NH bonds in the 1*H*-1,2,4-triazole-1-carboxamidine cation.

Single-crystals of **2** suitable for X-ray diffraction were obtained directly from the original reaction mixture without the need of recrystallization. An X-ray diffraction study of **2** revealed that the compound crystallizes in the monoclinic space group P2<sub>1</sub>/c with no water of crystallization. Figure 7 shows the molecular structure of **2** along with selected bond lengths and angles. Crystallographic data and structure refinement details are found in Table 1.



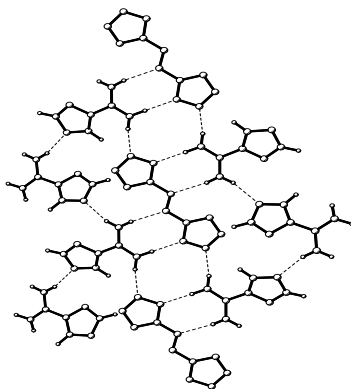
**Figure 7.** Molecular structure of **2** in the crystal, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): C(4)–N(6) 1.4042(18), C(4)–N(7) 1.3334(19), C(1)–N(10) 1.3344(18), N(1)–C(1)–N(2) 125.73(9), N(1)–C(1)–N(3) 118.75(9), N(2)–C(1)–N(3) 116.02(9), N(3)–C(2)–N(5) 109.42(9), N(5)–C(2)–H(2) 128.20(8), N(3)–C(2)–H(2) 122.40(8), N(4)–C(3)–N(5) 115.05(9), N(4)–C(3)–H(3) 119.90(8), N(5)–C(3)–H(3) 125.10(8) (#1  $-x + 3, -y, -z + 1$ ).

Once again, the structural parameters in the cations and anion in **2** were found to be unexceptional and in close agreement with those of previously reported azotetrazolates. The central N=N distance in the azotetrazolate dianion is 1.2601(18) Å. Like many previously reported azolium azotetrazolate salts [23–32], the crystal structure of **2** is characterized by layers interconnected through an array of hydrogen bonds. Figure 8 shows a packing diagram of compound **2**.



**Figure 8.** Packing diagram of 1*H*-1,2,4-triazole-1-carboxamidinium-5,5'-azotetrazolate (**2**). Dashed lines represent hydrogen bonds.

Unlike compound **1**, the crystal structure of **2** contains no water of crystallization despite the fact that the bulk material was isolated from aqueous solution. Figure 9 illustrates in more detail how the layers are formed through different N–H...N hydrogen bonds not only between cations and anions but also between adjacent cations. Two tetrazole ring nitrogen atoms as well as the N atoms of the central azo group in the 5,5'-azotetrazolate dianion are engaged in the N–H...N hydrogen bonds to the C(NH<sub>2</sub>)<sub>2</sub> amidinium hydrogens of the cations. Interestingly, one amidinium hydrogen of the cationic C(NH<sub>2</sub>)<sub>2</sub> moiety also forms a N–H...N hydrogen bond to a triazole ring-N atom of a neighbouring 1*H*-1,2,4-triazole-1-carboxamidinium cation. Details of the hydrogen bonding in the solid-state structure of **2** are summarized in Table 3.



**Figure 9.** N–H...N hydrogen bonding in the crystal structure of 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (**2**).

**Table 3.** Hydrogen bond lengths [Å] in **2**.

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(2)–H(2NA)...N(5)#2	0.870(15)	2.139(15)	2.9883(13)	165.0(13)
N(1)–H(1NA)...N(10)#3	0.944(16)	1.936(16)	2.8802(15)	178.3(14)
N(2)–H(2NB)...N(6)#3	0.865(17)	2.179(17)	3.0336(15)	169.4(14)
N(2)–H(2NB)...N(7)#2	0.865(17)	2.574(16)	3.0965(13)	119.8(12)
N(1)–H(1NB)...N(9)#4	0.904(15)	1.986(16)	2.8752(14)	167.5(14)

#1  $-x + 1, -y + 1, -z$ ; #2  $-x + 2, y + 1/2, -z + 1/2$ ; #3  $x + 1, -y + 3/2, z + 1/2$ ; #4  $-x + 2, y - 1/2, -z + 1/2$ .

### 2.3. Sensitivity Tests

The methods for testing primary explosives have recently been summarized in a very informative short review article by Mehta *et al.* [34]. Primary explosives are compounds which are very sensitive to small stimuli such as impact, friction, electrostatic discharge, and heat, so that very little energy is needed to initiate such materials. Materials that are more sensitive than PETN (pentaerythritol tetranitrate) are generally considered primary explosives [3]. Primary explosives are usually employed in milligram quantities to initiate large amounts of less sensitive materials such as secondary explosives (TNT (2,4,6-trinitrotoluene), RDX (1,3,5-trinitrohexahydro-s-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) *etc.*) or propellants [34]. Typical primary explosives are e.g., lead(II) azide,  $\text{Pb}(\text{N}_3)_2$  [35] and several forms of lead(II) styphnate (lead(II) trinitroresorcinate) [3].

For initial safety testing, the impact and friction sensitivities of the new azotetrazolates were tested according to established BAM methods [3] using a BAM drophammer and BAM friction tester. Figures 10 and 11 show the devices used in this study. In addition, a simple combustion test was carried out. The results are summarized in Table 4. The tetraphenylphosphonium salt **1** was found to be insensitive towards impact ( $i > 40$  J) and friction ( $f > 360$  N) and showed no deflagration upon combustion. 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (**2**) was also found to be insensitive to friction ( $> 360$  N) but with a value of  $i = 10$  J it was found to be significantly impact-sensitive. It also showed deflagration in the combustion test. In order to assess the energetic properties of the materials described in this study, it is useful to compare the found sensitivity data with those reported for a common secondary explosive such as TNT (trinitrotoluene). With a value of  $i = 10$  J, the 1*H*-1,2,4-triazole-1-



carboxamidine salt **2** is more impact-sensitive than TNT ( $i = 15$  J) and relatively insensitive to friction (TNT:  $f = 355$  N) [3,36]. On the other hand, compound **2** is slightly less sensitive to impact than typical primary explosives such as than lead(II) styphnate ( $i = 2.5$ – $5.0$  J) or lead(II) azide ( $i = 3.0$ – $6.5$  J) [3,36]. The reason for the differences in the energetic properties between **1** and **2** can be seen in the fact that **2** is a nitrogen-rich azotetrazolate salt (N-content 73.14%), while compound **1** is not (N-content 16.62%). This can also be described as a “dilution” of the nitrogen-rich azotetrazolate dianions by the bulky tetraphenylphosphonium cations in the crystalline state of **1**. In both cases, long-term stability tests over a period of 30 days showed no changes in these sensitivity data.

**Table 4.** Energetic properties of **1** and **2**.

Compound	1	2
M (g/mol)	914.93	406.33
$\rho$ g/cm <sup>3</sup>	1.294	1.657
Impact sensitivity $i$ (J)	> 40	10
Friction Sensitivity $f$ (N)	> 360	> 360
Combustion Test	combustion	deflagration
N-content (%)	16.62	73.14
Oxygen balance $\Omega$ (%)	−242.9	−90.64



**Figure 10.** BAM drophammer setup used in this study.



**Figure 11.** BAM friction test setup used in this study.

### 3. Experimental Section

The starting material  $\text{Na}_2\text{C}_2\text{N}_{10}\cdot 5\text{H}_2\text{O}$  was prepared according to the original protocol described by Thiele [7]. Commercially available  $[\text{PPh}_4]\text{Cl}$  (Aldrich) was used as received. 1*H*-1,2,4-triazole-1-carboxamidine-hydrochloride (or 1-amidino-1,2,4-triazole-hydrochloride, CAS-No. 19503-26-5) was a gift from DEGUSSA GmbH (Degussa AG, Trostberg, Germany). The X-ray diffraction data for compounds **1** and **2** were measured at  $-173\text{ }^\circ\text{C}$  on a STOE IPDS diffractometer (STOE & Cie GmbH, Darmstadt, Germany). Structure solution and refinement were carried out using the programs SHELXS-97 [37] and SHELXL-97 [38].

#### 3.1. Preparation of Tetraphenylphosphonium-5,5'-azotetrazolate (**1**)

To a saturated solution of 0.30 g (1.0 mmol)  $\text{Na}_2\text{C}_2\text{N}_{10}\cdot 5\text{H}_2\text{O}$  in warm ( $40\text{ }^\circ\text{C}$ ) water was added a concentrated aqueous solution of tetraphenylphosphonium chloride (0.75 g, 2.0 mmol). Within a few minutes, compound **1** precipitated as a crystalline, bright yellow solid. Yellow single-crystal suitable for X-ray diffraction were obtained by recrystallization from a minimum amount of hot reagent grade acetone. Yield: 0.71 g (78%), m.p.  $254\text{ }^\circ\text{C}$ . Anal. calcd. for  $\text{C}_{50}\text{H}_{40}\text{N}_{10}\text{P}_2\cdot 4\text{H}_2\text{O}$  (914.93 g/mol): C 65.64, H 5.29, N 15.31%; found: C 64.69, H 4.95, N 15.16%.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 400 MHz):  $\delta$  7.95 (8 H, m, *p*-H), 7.83–7.67 (32 H, m, *o*-H, +*m*-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{DMSO}-d_6$ , 100 MHz):  $\delta$  173.1 ( $[\text{N}_4\text{C}=\text{N}=\text{N}-\text{CN}_4]^{2-}$ ), 135.2 (*p*-C), 134.1 (*o*-C), 128.5 (*m*-C), 118.1 (*ipso*-C).  $^{31}\text{P}$ -NMR ( $\text{DMSO}-d_6$ , 162 MHz, 35%  $\text{H}_3\text{PO}_4$ ):  $\delta$  23.0. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  3730 (m), 3055(m), 2141 (w), 2005 (w), 1829 (w), 1627 (w), 1584 (m), 1481 (m), 1436 (m), 1374 (s), 1315 (m), 1184 (m), 1172 (m), 1145 (m), 1107 (s), 1024 (m), 997 (m), 857 (w), 763 (m), 753 (m), 724 (s), 692 (m), 554 (w), 528 (s), 464 (m).

#### 3.2. Preparation of 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (**1**)

To a saturated solution of 1.00 g (3.3 mmol)  $\text{Na}_2\text{C}_2\text{N}_{10}\cdot 5\text{H}_2\text{O}$  in warm ( $40\text{ }^\circ\text{C}$ ) water (10 mL) was added a concentrated aqueous solution (10 mL) of 1*H*-1,2,4-triazole-1-carboxamidine hydrochloride (0.48 g, 3.3 mmol). After short standing at r.t., a copious amount of bright yellow crystals of compound **2** formed. Selected crystals obtained in this way were directly suitable for X-ray diffraction. Yield: 1.15 g (86%), m.p.  $154.2\text{ }^\circ\text{C}$ . Anal. calcd. for  $\text{C}_8\text{H}_{14}\text{N}_{20}\text{O}$  (406.33 g/mol): C 23.65, H 3.47, N 68.95%; found: C: 23.74, H 3.01, N: 70.14%.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , 400 MHz):  $\delta$  8.29 (s, 2 H, N–H), 2.49 (s, 4 H,  $\text{C}(\text{NH}_2)_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (20 $^\circ\text{C}$ ;  $\text{DMSO}-d_6$ , 100 MHz):  $\delta$  153.2 ( $[\text{N}_4\text{C}=\text{N}=\text{N}-\text{CN}_4]^{2-}$ ), 149.8 ( $\text{C}=\text{N}$ ), 144.5 ( $\text{C}(\text{NH}_2)_2$ ). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{max}}$  3851 (w), 3747 (w), 3127 (vs), 3109 (vs), 3007 (vs), 2329 (m), 2216 (m), 2072 (m), 2051 (m), 1875 (m), 1724 (vs), 1651 (m), 1529 (vs), 1517 (vs), 1455 (m), 1393 (vs), 1345 (m), 1293 (m), 1227 (m), 1194 (vs), 1162 (m), 1134 (m), 1112 (m), 1103 (m), 1073 (m), 1046 (m), 1030 (m), 980 (vs), 960 (m), 941 (m), 870 (m), 837 (m), 786 (m), 763 (m), 739 (s), 710 (s), 692 (s), 667 (m), 623 (m), 570 (m), 528 (m), 464 (m), 455 (m).

### 4. Conclusions

In summarizing the results reported here, two new azotetrazolate salts, namely tetraphenylphosphonium-5,5'-azotetrazolate (**1**) and 1*H*-1,2,4-triazole-1-carboxamidine-5,5'-azotetrazolate (**2**), have been prepared and structurally authenticated through single-crystal X-ray

diffraction. Both are characterized by hydrogen bond networks in the solid state. Particularly, the 1*H*-1,2,4-triazole-1-carboxamidine derivative **2** is easily crystallized and isolated in high yield (86%). Due to its high nitrogen-content of 73.14%, compound **2** is significantly impact-sensitive.

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### Author Contributions

R.D. carried out the experiments; C.G.H. carried out the crystal structure determinations; F.T.E. conceived and supervised the experiments and wrote the paper.

### Conflicts of Interest

The authors declare no conflict of interest.

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