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# Bistetrazoles: Nitrogen-Rich, High-Performing, Insensitive Energetic Compounds

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Large-scale syntheses of nitrogen-rich 5,5′-hydrazinebistetrazole (**HBT**) (or 1,2-ditetrazolylhydrazine) and bis(3,4,5-triamino-1,2,4-triazolium) 5,5′-azotetrazolate (**G$_2$ZT**) with high yields and purities on a multigram scale are introduced. DSC analysis showed good thermal stabilities for both materials (>200 °C) and their long-term stabilities were assessed by TSC (thermal safety calorimetry). Because molecular structures play an important role in the properties of an energetic material, hydrogen bonding in both compounds is described in terms of graph-set analysis. The extensive hydrogen bonding in the structures seems to account for their relatively high densities (**HBT**, $\rho = 1.841$ g cm$^{-3}$; and **G$_2$ZT**, $\rho = 1.708$ g cm$^{-3}$). The heats of combustion of the two compounds were calculated ($\Delta_c U°$(**HBT**) $= -2396$ cal g$^{-1}$ and $\Delta_c U°$(**G$_2$ZT**) $= -2775$ cal g$^{-1}$) and combined with the experimentally determined densitites (X-ray) and the molecular formulas to calculate the detonation pressures ($P$) and velocities ($D$) using the EXPLO5 computer-code (**HBT**, $P = 27.7$ GPa, $D = 8523$ m s$^{-1}$; and **G$_2$ZT**, $P = 19.9$ GPa, $D = 7683$ m s$^{-1}$). The sensitivity of both materials to shock, friction and electrostatic discharge was assessed using standard BAM tests, revealing very stable compounds (**HBT**, shock >30 J, friction >108 N; and **G$_2$ZT**, shock >30 J, friction >360 N) with no sensitivity toward an electrostatic discharge of ~20 kV. In addition, the explosion/decomposition gases were experimentally measured by means of IR spectroscopy and mass spectrometry and are compared with the explosion/decomposition gases calculated using the ICT thermodynamic code. With high nitrogen contents (~80%), the reported bistetrazoles are prospective new, environmentally friendly, high-performance energetic materials with low sensitivities and good thermal stabilities that might find use as solid propellants or in propellant charges.

## Introduction

The synthesis and study of nitrogen-rich energetic compounds and highly energetic materials for possible military application has been a long-term goal in our group.[1–3] Nitrogen-rich, high-energy-density materials (HEDMs) derive most of their energy from their high positive heats of formation (the number of nitrogen atoms linked together is directly proportional to the performance of the compound) [4,5] in contrast to classical explosives [6,7] such as 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazinane (RDX), and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX)[8] (Figure 1) that derive their energy from oxidation of the carbon backbone. On the other hand, compounds such as 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX) or 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) are HEDMs that release additional energy upon detonation as a consequence of the cage-strain found in these systems. The principal problems associated with the use of the above-mentioned materials are the environmentally detrimental gases (i.e., NO$_x$ gases) formed upon decomposition and the fact that the performance of a material is often associated with high sensitivity to shock or friction, making handling of the compound troublesome. In this context, there are criteria, which new HEDMs should meet[9] in order to be considered possible replacements for commonly used ener-

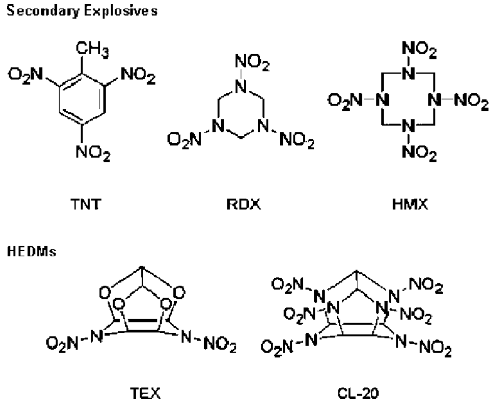

**Figure 1.** Structures of commonly used secondary explosives and high-energy-density materials (HEDMs).

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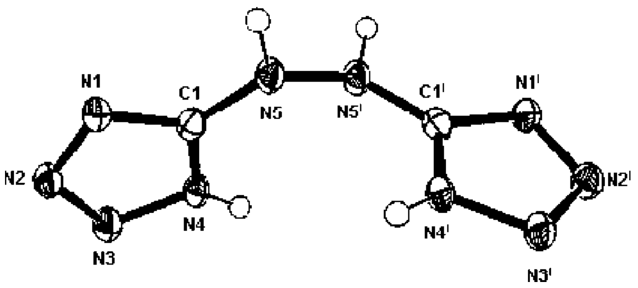


**Figure 2.** Molecular structure of **HBT** (half of the molecule is generated by symmetry, symmetry code: (i) $1 - x$, $y$, $2.5 - z$); Ortep picture with thermal ellipsoids set at 50% probability. Selected bond lengths (Å) and angles (deg): N3−N2 1.288(2), N3−N4 1.362(2), N2−N1 1.365(2), N4−C1 1.333(2), N1−C1 1.327(2), N5−C1 1.356(2), N5−N5$^{i}$ 1.391(2); N2−N3−N4 105.7(2), N3−N2−N1 111.8(1), C1−N4−N3 108.5(1), C1−N5−N5$^{i}$ 116.8(1), N5$^{i}$−N5−H5 116.7(1), C1−N1−N2 104.9(1), N1−C1−N4 109.0(1), N1−C1−N5 124.1(1), N4−C1−N5 126.7(1).

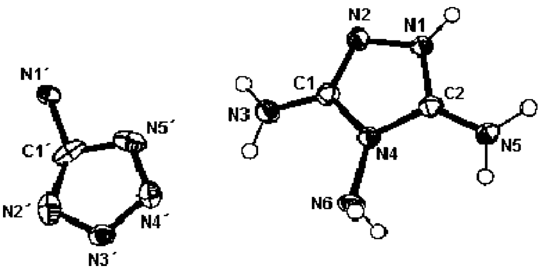


**Figure 3.** Molecular structure of **G$_2$ZT** (half of the molecule is generated by symmetry, symmetry code: (i) $-1 - x$, $1 - y$, $-1 - z$); Ortep picture with thermal ellipsoids set at 50% probability. Selected bond lengths (Å) and angles (deg): C1−N2 1.312(2), C1−N3 1.330(2), C1−N4 1.377(2), C2−-N1 1.325(2), C2−N5 1.315(2), C2−N4 1.360(2), N6−N4 1.394(2), N1−N2 1.402(2), C1′−N2′ 1.324(2), N5′−C1′ 1.323(3), N2′−N3′ 1.326(2), N4′−N3′ 1.314(2), N4′−N5′ 1.334(2), C1′−N1′ 1.464(7); N2−C1−N3 127.6(2), N2−C1−N4 111.2(2), N3−C1−N4 121.2(2), N1−C2−N5 129.3(2), N1−C2−N4 105.6(2), N5−C2−N4 125.1(2), C2−N1−N2 112.0(1), C1−N4−C2 107.6(1), C1−N4−N6 123.6(1), C1−N4−N6 128.6(1), C1−-N2−N1 103.6(1), C1′−N5′−N4′ 103.9(2), C1′−N2′−-N3′ 103.9(2), N4′−N3′−N2′ 109.8(2), N3′−N4′−N5′ 109.3(1), N5′−C1′−N2′ 112.9(2), N5′−C1′−N1′ 103.5(3), N2′−C1′−N1′ 143.5(3).

getic compounds such as RDX or HMX. Ideally, new compounds should have detonation velocities ($D$) greater than 8500 m s$^{-1}$ ($D_{\mathrm{RDX}} = 8800$ m s$^{-1}$),[10] a critical diameter of at least 8 mm in the Koenen (steel sleeve) test, good thermal stabilities ($T_d \geq 200$ °C), they should be hydrolytically stable with shelf lives longer than 15 years, be compatible with the binder and/or plasticizer, insensitive to shock (>7 J) and friction (>120 N), have low (no) solubility in water, the decomposition products should be environmentally benign and the yield for its synthesis should be high and the associated cost low.

The performance of an energetic material is largely a function of its oxygen balance (composition), density, and heat of formation, of which the two last are governed to some extent by the molecular structure.[11] One way of counteracting the aforementioned correlation of high performance with high sensitivity to friction and shock is the use of systems, which form extensive hydrogen-bonding networks in the solid state.[12] Such hydrogen-bonded networks help to stabilize the material substantially. On the other hand, the higher the nitrogen content of a material, the higher its heat of formation[13] and thus performance. In this context, we are interested in azole-based energetic materials with respect to our ongoing interest in nitrogen-rich compounds as ingredients for propellants and explosives formulations[14,15] and are seeking new energetic compounds with high densities.[16,17] Tetrazole-based energetic materials have proven to be unique[18–20] in that they combine a nitrogen-rich moiety, which also provides the compounds with relatively high densities, good thermal stabilities, and low sensitivities.

Herein, we describe a large-scale synthesis for the formation of two high-performance insensitive energetic materials, namely, 5,5′-hydrazinebistetrazole (**HBT**)[21] (or 1,2-ditetrazolylhydrazine) and bis(3,4,5-triamino-1,2,4-triazolium) 5,5′-azotetrazolate (**G$_2$ZT**),[22] which yield the compounds on a multigram scale in excellent yields. The detonation properties of the two compounds were calculated from experimentally measured constant volume energies of combustion and the decomposition gases formed upon explosion were both determined experimentally and calculated. Lastly, the stability/compatibility, sensitivity, solubility, performance, etc., of the two compounds are discussed in basis of the criteria for new energetic materials mentioned above.

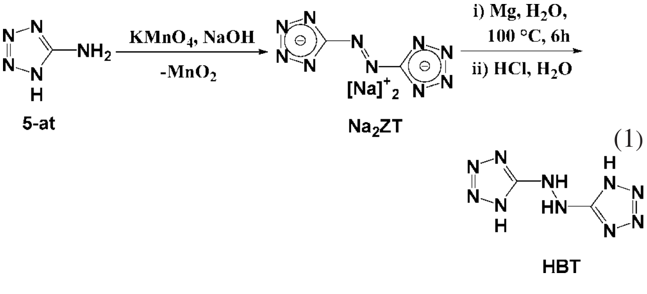
**Table 1. Selected Hydrogen Bonds for HBT and G$_2$ZT (distances in Å, angles in deg; see Figures 2 and 3 for the numbering schemes, respectively)**

| D−H···A | D−H | H···A | D−H···A | D−H−A |
|---|---|---|---|---|
| | | **HBT**[a] | | |
| N4−H4···N2$^{i}$ | 0.81(2) | 2.13(2) | 2.917(2) | 166.(2) |
| N5−H5···N1$^{ii}$ | 0.86(2) | 2.09(2) | 2.941(2) | 168.(2) |
| | | **G$_2$ZT**[b] | | |
| N3−H2···N6 | 0.91(2) | 2.550(2) | 2.837(3) | 99(2) |
| N6−H6···N2$^{i}$ | 0.88(2) | 2.45(2) | 3.277(2) | 157(2) |
| N3−H1···N2$^{ii}$ | 0.88(2) | 2.12(2) | 2.981(2) | 165(2) |

[a] Symmetry codes for **HBT**: (i) $x$, $-y$, $2.5 + z$; (ii) $1 - x$, $-1 - y$, $2 - z$. [b] Symmetry codes for **G$_2$ZT**: (i) $1 + x$, $y$, $z$; (ii) $-1 - x$, $1 - y$, $-z$.

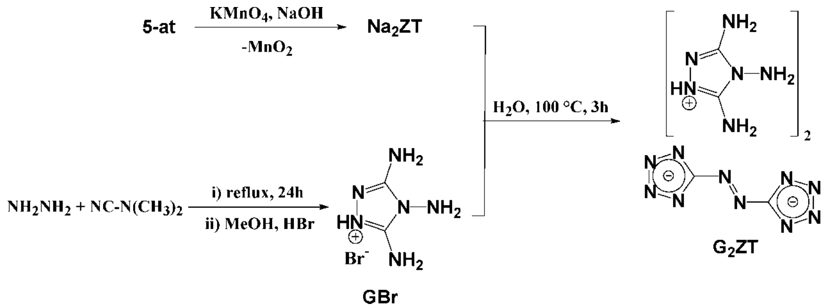
## Synthesis

**5,5′-Hydrazinebistetrazole (HBT).** Commercially available 5-amino-*1H*-tetrazole (5-AT) was oxidized in sodium hydroxide solution with potassium permanganate yielding sodium 5,5′-azotetrazolate pentahydrate (Na$_2$ZT),[23] which was isolated and reacted overnight with an excess of magnesium powder in aqueous solution and subsequently treated with hydrochloric acid yielding 5,5′-hydrazinebistetrazole (**HBT**),[21,24] which precipitated as a white powder upon cooling (eq 1).



(1)

**Bis(3,4,5-triamino-1,2,4-triazolium) 5,5′-Azotetrazolate (G$_2$ZT).** A solution of sodium 5,5′-azotetrazolate pentahydrate (Na$_2$ZT), prepared as described above,[23] was reacted with 3,4,5-triamino-1,2,4-triazolium (guanazinium) bromide (GBr), synthesized from aqueous hydrazine and dimethylcyanamide[22] and subsequent acid workup. After the reaction mixture was boiled for 1 h in water, bis(3,4,5-triamino-1,2,4-triazolium) 5,5′-azotetrazolate (**G$_2$ZT**) formed as a yellow insoluble powder (eq 2).



(2)

Both compounds (**HBT** and **$G_2ZT$**) were found to be analytically pure on the basis of a CHN analysis (±0.5%).

## Molecular Structures and Hydrogen Bonding

Figures 2 and Figures 3 show Ortep pictures of the asymmetric units of **HBT** and **$G_2ZT$**, as well as the bonding parameters and the labeling schemes. A full description of the structures has been published elsewhere.[21,22] The scope of this section is to try to establish a connection between the extensive hydrogen-bonding found in **HBT** and **$G_2ZT$** and their high densities and explosive performance.

As mentioned in the introductory section, hydrogen bonding is an important consideration in the synthesis of new energetic materials because the more extensive it is, the higher the density of a material, which, in turn, increases the performance (detonation parameters) of the same. As expected from the substantial number of electronegative (nitrogen) atoms readily available to form hydrogen bonds in **HBT** and **$G_2ZT$**, both compounds form complicated networks linked together by $N-H\cdots N$ interactions. A sample of the hydrogen bonds found in the crystal structures of the two compounds subject of this study is tabulated in Table 1.

Figure 4 shows the hydrogen bonds formed between **HBT** molecules. Only two crystallographically independent (strong) hydrogen bonds ($N4-H4\cdots N2^{i} = 2.917(2)$ Å and $N5-H5\cdots N1^{ii} = 2.941(2)$ Å; symmetry codes: (i) $1 + x, y, z$; (ii) $-1 - x, 1 - y, -z$) are formed (Table 1) but every molecule participates in up to eight hydrogen bonds with N3 being the only electronegative atom that does not form any significant interaction. The nomenclature introduced by Bernstein et al.[25] in combination with the computer-program RPLUTO[26] are useful to explain the relatively complicated hydrogen-bonding networks found in the crystal structure of **HBT**. Apart from very many chain patterns (**C1,1(4C1,1(5)** and ***C*2,2(7)**), **HBT** participates in the formation of ring graph-sets, the most important ones being an **R2,2(8)** motif by using N1 and N5 and a larger **R2,2(16)** pattern including N2, N1, N5, N5$^{i}$, N4$^{i}$, N2$^{vi}$, and N4$^{vii}$ (symmetry codes: (i) $1 - x, y, 2.5 - z$; (vi) $1 - x, -y, 2 - z$; (vii) $x, -y, -0.5 + z$).

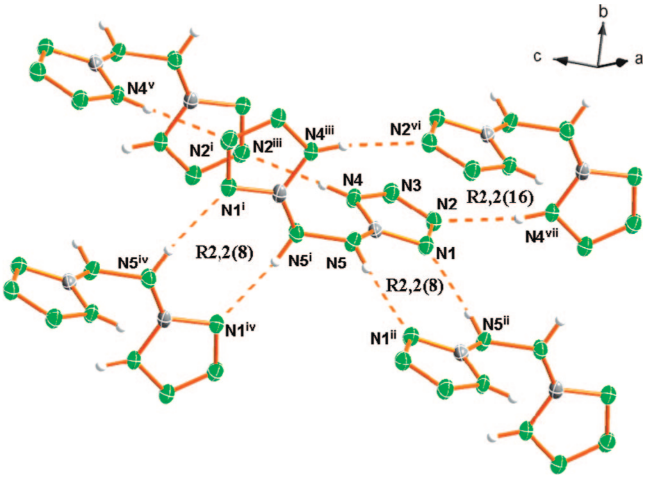


**Figure 4.** Hydrogen bonding around the molecule in the crystal structure of **HBT** (diamond picture, symmetry codes: (i) $1 - x, y, 2.5 - z$; (ii) $1 - x, -1 - y, 2 - z$; (iii) $x, -y, 0.5 + z$; (iv) $x, -1 - y, 0.5 + z$; (v) $1 - x, -y, 3 - z$; (vi) $1 - x, -y, 2 - z$; (vii) $x, -y, -0.5 + z$).

In **$G_2ZT$**, the structure also contains multiple hydrogen bonds, which are difficult to describe due to the disorder found in the azotetrazolate anion, thus a description of the hydrogen bonding involving the anion is omitted. However, the cation forms up to five hydrogen bonds (see Figure 5) with other cations, one of which is intramolecular ($N3-H2\cdots N6$

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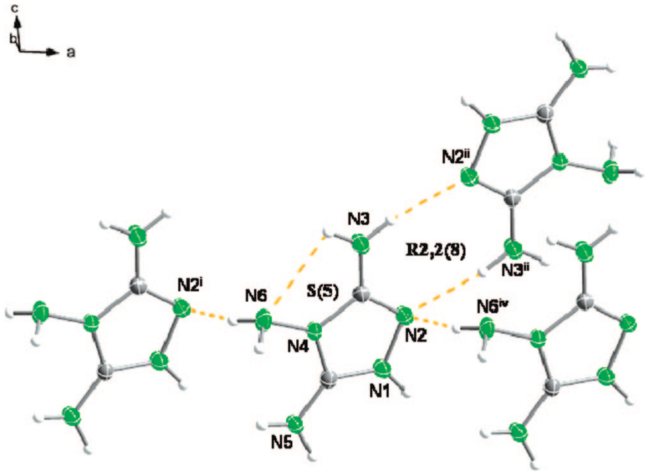

**Figure 5.** Hydrogen bonding around the guanazinium cation in the crystal structure of **$G_2ZT$** (the hydrogen bonds formed with the disordered azotetrazolate anion have been omitted. Diamond picture, symmetry codes: (i) $1 + x, y, z$; (ii) $-1 - x, 1 - y, -z$; (iii) $-1 + x, y, z$).

= 2.837(3) Å). N2 and N6 are involved in a long hydrogen bond between layers ($N6-H6\cdots N2^i$ = 3.277(2) Å; symmetry code: (i) $1 + x, y, z$), whereas N2 and N3 link with $N3^{ii}$ and $N2^{ii}$, respectively, forming cation dimer pairs ($N3-H1\cdots N2^{ii}$ = 2.981(2) Å; symmetry code: (ii) $-1 - x, 1 - y, -z$). Using graph-set nomenclature, the intramolecular hydrogen bond found in the cation can be described as a common[22,27,28] **S(5)** motif at the primary level, whereas the dimer-pairs formed by N2 and N3 describe a ring pattern with the label **R2,2(8)** (also at the primary level). The formation of the **R2,2(8)** dimer-pairs is common for guanazinium salts.[22,27] The three amino groups in the cation allow for the formation of a very dense structure ($\rho$ = 1.708 g $cm^{-3}$) in comparison to other 5,5′-azotetrazolate salts, which, in the rule, have densities between 1.45 and 1.55 g $cm^{-3}$ [15b,29,30] or at best around 1.6 g $cm^{-3}$, in the case of salts with counterions that have the possibility of forming a significant number of hydrogen bonds such as the triaminoguanidinium cation.[31]

## Explosive Properties

Data collected for friction, impact, and electrostatic discharge sensitivity are summarized in Table 2. None of the compounds showed sensitivity toward shock. No detonation was observed in the drop hammer test (>30 J) nor in the friction tester (>360 N).[32–34] In addition, each compound was roughly tested for sensitivity to electrostatic discharge by spraying sparks across a small (a few crystals) sample of material using a tesla coil (ESD testing ~20 kV). A comparison with the properties of common explosives is useful to asses the energetic compounds in this study. Both **HBT** and **$G_2ZT$** are less sensitive to friction (*f*) and shock (*s*) than RDX or HMX (both $f = 120$ N and $s = 7.4$ J) and CL-20 ($f = 48$ N and $s = 4$ J).[35] This is to be expected because extensive hydrogen-bonding helps to stabilize a material and interesting since the two tunable properties of which the performance of a material is dependent (density and heat of formation) are generally increased and slightly decreased (less positive), respectively. Because the performance of an energetic material is most heavily dependent on density, increases in this property tend to outweigh the adverse affect on heat of formation caused by strong hydrogen-bonding.[35] This is the principal reason why compounds that can form multiple hydrogen bonds are of interest as prospective insensitive materials with high densities and performances.[36,37] The compounds under study were also less sensitive to friction and electrostatic discharge than RDX, HMX, and CL-20.[35] Lastly, the materials reported here are safe for transport under the UN Recommendations on the Transport of Dangerous Goods as described in ref 32.

In addition to safety considerations, performance of high-energy-density materials is also of considerable interest. Using the molecular formula, density (from X-ray), and energy of formation ($\Delta_f U°$), we can use the EXPLO5 computer code[38] to calculate the detonation velocities and pressures of CHN(O)-based explosive materials. The following values for the empirical constants in the Becker–Kistiakowsky–Wilson equation of state (BKWN-EOS) were used: $\alpha = 0.5$, $\beta = 0.176$, $\kappa = 14.71$, and $\theta = 6620$. The detonation parameters for **HBT** and **$G_2ZT$** are presented in Table 2.

The physiochemical properties of both compounds are tabulated in Table 3. Both compounds have high nitrogen contents (**HBT**, 83.3%; **$G_2ZT$**, 78.2%) and highly negative oxygen balances ($\Omega$, **HBT**, −57.1%; **$G_2ZT$**, −77.1%) similar to TNT ($\Omega = -74.0\%$). The density for **HBT**, from the X-ray measurement, is in analogy to that of **$G_2ZT$** (see hydrogen-bonding discussion), exceptionally high in comparison to the parents 5-amino-*1H*-tetrazole[39] and 1-5-

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(32) Impact: insensitive >40 J, less sensitive ≥35 J, sensitive ≥4 J, very sensitive ≤3 J; friction: insensitive >360 N, less sensitive = 360 N, sensitive <360 N and >80 N, very sensitive ≤80 N, extremely sensitive ≤10 N; According to the UN Recommendations on the Transport of Dangerous Goods, (+) indicates not safe for transport.

(33) http://www.bam.de.

(34) Klapötke, T. M.; Rienäcker, C. M. *Propell. Explos. Pyrotech.* **2001**, *26*, 43–47.

(35) Köhler, J.; Meyer, R. *Explosivstoffe* 9th ed.; Wiley-VCH: Weinheim, Germany, 1998.

(36) Bemm, U.; Östmark, H. *Acta Crystallogr., Sect. C* **1998**, *54*, 1997–1999.

(37) Westwell, M. S.; Searle, M. S.; Wales, D. J.; Williams, D. H. *J. Am. Chem. Soc.* **1995**, *117*, 5013–5015.

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(39) Bray, D. D.; White, J. G. *Acta Crystallogr., Sect. B* **1979**, *35*, 3089–3091.

**Table 2. Initial Safety Testing Results and Predicted Energetic Performance of HBT and $G_2ZT$ Using the EXPLO5 Code**[a]

| | $T_{ex}$ (K)[b] | $V_0$ (L kg$^{-1}$)[c] | $P$ (GPa)[d] | $D$ (m s$^{-1}$)[e] | crit. diam. (mm)[f] | shock (J)[g] | friction (N)[g] | ESD (+/−)[h] |
|---|---|---|---|---|---|---|---|---|
| **HBT** | 2539 | 782 | 27.7 | 8523 | >8 | >30 | >108 | − |
| **$G_2ZT$** | 1892 | 805 | 19.9 | 7683 | 10 | >30 | >360 | − |

[a] See ref 21 (**HBT**) and ref 22 (**$G_2ZT$**). [b] Temperature of the explosion gases. [c] Volume of the explosion gases. [d] Detonation pressure. [e] Detonation velocity. [f] Critical diameter from Koenen (steel sleeve) test. [g] Shock and friction sensitivities. Tests according to BAM methods (see refs 32–34). [h] Rough sensitivity to electrostatic discharge: + sensitive, − insensitive.

**Table 3. Physiochemical Properties of Neutral HBT and Azotetrazolate Salt $G_2ZT$**

| | HBT | $G_2ZT$ |
|---|---|---|
| formula | $C_2H_4N_{10}$ | $C_6H_{14}N_{22}$ |
| mol mass (g mol$^{-1}$) | 168.12 | 394.33 |
| $T_d$ (°C)[a,b] | 208 | 212 |
| $\Delta H_{sub}$ (J mol$^{-1}$)[c] | 90 | |
| N (%)[d] | 83.3 | 78.2 |
| Ω (%)[e] | −57.1 | −77.1 |
| $\rho$ (g cm$^{-3}$)[f] | 1.841 | 1.708 |
| $\Delta_cU°$ (cal g$^{-1}$)[g] | −2396 [21] | −2775 [22] |
| $\Delta_fU°$ (kJ kg$^{-1}$)[h] | +2566 [21] | +1442 [22] |
| $\Delta_fH°$ (kJ kg$^{-1}$)[i] | +2463 [21] | +1329 [22] |

[a] Chemical melting point and from measurement with $\beta = 5$ °C min$^{-1}$. [b] Decomposition point (DSC onsets) from measurement with $\beta = 5$ °C min$^{-1}$. [c] Enthalphy of sublimation (for neutral compounds) calculated according to ref 37. [d] Nitrogen percentage. [e] Oxygen balance according to ref.[43] [f] Density from X-ray measurements. [g] Enthalpy of combustion. [h] Energy of formation; [i] Enthalpy of formation.

**Table 4. Explosive Properties of HBT and $G_2ZT$ and Comparison with Common High Explosives and Formulations with Commonly Used Oxidizers and High Explosives (calculated using the EXPLO5 code)**

| compd | ratio (%)[a] | Ω (%)[b] | $\rho$ (g cm$^3$)[c] | $P$ (GPa)[d] | $D$ (m s$^{-1}$)[e] |
|---|---|---|---|---|---|
| **HBT** | 100 | −57.1 | 1.841 | 27.7 | 8523 |
| **$G_2ZT$** | 100 | −77.1 | 1.708 | 19.9 | 7683 |
| TNT | 100 | −74.0 | 1.654 | 20.5 | 7171 |
| picric acid | 100 | −45.4 | 1.767 | 24.9 | 7660 |
| TEX | 100 | −42.7 | 1.990 | 30.8 | 8231 |
| RDX | 100 | −21.6 | 1.800 | 34.0 | 8885 |
| HMX | 100 | −21.6 | 1.905 | 38.2 | 9216 |
| CL-20 | 100 | −11.0 | 2.020 | 44.5 | 9632 |
| **HBT** + AN | 26:74 | −0.1 | 1.753 | 26.5 | 8278 |
| **HBT** + ADN | 31:69 | +0.1 | 1.818 | 33.5 | 9014 |
| **$G_2ZT$** + AN | 21:79 | −0.4 | 1.719 | 24.5 | 8029 |
| **$G_2ZT$** + ADN | 25:75 | +0.1 | 1.783 | 31.4 | 8788 |

[a] Percentage of compound (**HBT** or **$G_2ZT$**) and either oxidizer (AN, ADN). [b] Oxygen balance (EXPLO5). [c] Density (EXPLO5). [d] Detonation pressure. [e] Detonation velocity.

diamino-*1H*-tetrazole,[40] which have density values ~0.3 g cm$^{-3}$ lower.

The energies of formation ($\Delta_fU°$) of both compounds were back-calculated from the heat of combustion on the basis of their combustion equations (eq 3), Hess's Law, the known standard heats of formation for water and carbon dioxide[41] and a correction for change in gas volume during combustion. The ecalculated $\Delta_fU°$ (back-calculated from $\Delta_cU°$) for both materials take highly positive values (**HBT**: +2566 kJ kg$^{-1}$ and **$G_2ZT$**: +1442 kJ kg$^{-1}$) and their heats of formation are, however, lower than that of bishydrazinium 5,5′-azotetrazolate, for which $\Delta H°_f \approx 3700$ kJ kg$^{-1}$.[42]

$$\textbf{HBT}:\quad C_2H_4N_{10}(s) + 3O_2 \rightarrow 2CO_2 + 2H_2O(l) + 5N_2(g)$$

$$\textbf{G}_2\textbf{ZT}:\quad [C_2H_7N_6]^+{}_2[C_2N_{10}]^{2-}(s) + 19/2O_2 \rightarrow 6CO_2(g) + 7H_2O(l) + 11N_2(g) \quad (3)$$

Because of the negative oxygen balances of both materials studied here,[43] it is of interest to study the performance of mixtures with an oxidizer. Formulations of **HBT** with different oxidizers such as ammonium nitrate (AN) or ammonium dinitramide (ADN) (Table 4). The best values were calculated for a mixture of **HBT** with ADN in an approximately oxygen neutral ratio ($D = 9014$ m s$^{-1}$ and $P = 33.5$ GPa), still in the range of performance calculated for HMX or RDX. On the other hand, formulations of **$G_2ZT$** with the oxidizers and high explosives listed above showed, in some instances, an increase in performance with respect to the stand-alone energetic material. Of the oxidizers used to calculate the mixtures, ADN was the only one capable of significantly increasing the detonation velocity and pressure ($D = 8788$ m s$^{-1}$ and $P = 31.4$ GPa).

The thermal and explosive properties of HBT and various salts (barium, lead and mercury) have been studied previously[44,45] with respect to their potential use as primary explosives. The authors discussed the results of the thermal decomposition studies on 5,5′-hydrazotetrazole (HBT) and its barium, lead and mercury salts. The decomposition data indicated that among the hydrazotetrazoles studied, the Pb salt was the least-stable compound. These studies showed that the lead compound is the most powerful primary explosive among the four compounds investigated.[44]

Apart from the detonation parameters calculated using the EXPLO5 computer-code, another method of assessing the performance of a material in a more practical way is the Koenen (steel-sleeve) test,[46] in which the sensitivity of a material to intense heat under confinement is tested. Figure 6 shows pictures for a Koenen test with a port diameter of 8 mm on 15 g of **HBT**. As expected from the high detonation parameters of the compound, the sleeve was completely destroyed by the explosion. RDX and HMX show similar behavior under the same test using the same critical diameter.[35] On the other hand, although **$G_2ZT$** exploded when using port sizes of 10 and 8 mm, resulting in 3 and 4 fragments of the steel-sleeve, respectively (at least 3 fragments are necessary to be able to consider it an explosion), many grams of the yellow compound were found on the test-bench after the explosion, which means that the reaction was not complete and a much better performance could poten-

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(40) Lyakhov, A. S.; Gaponik, P. N.; Voitekhovich, S. V. *Acta Crystallogr., Sect. C* **2001**, *57*, 185–186.

(41) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated*; National Bureau of Standards: Washington, D.C., 1972; Vol. 1.

(42) Singh, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3584–3601, and references therein.

(43) Calculation of the oxygen balance: $\Omega(\%) = (O-2C-H/2-xAO)\,1600/M$; $M$ = molecular mass.

(44) Reddy, G. Om.; Chatterjee, A. K. J. *Hazard. Mater.* **1984**, *9* (3), 291–303.

(45) De Yong, L. V.; Campanella, G. *J. Hazard. Mater.* **1989**, *21* (2), 125–33.

(46) http://www.sms-ink.com/products_koenen.html.

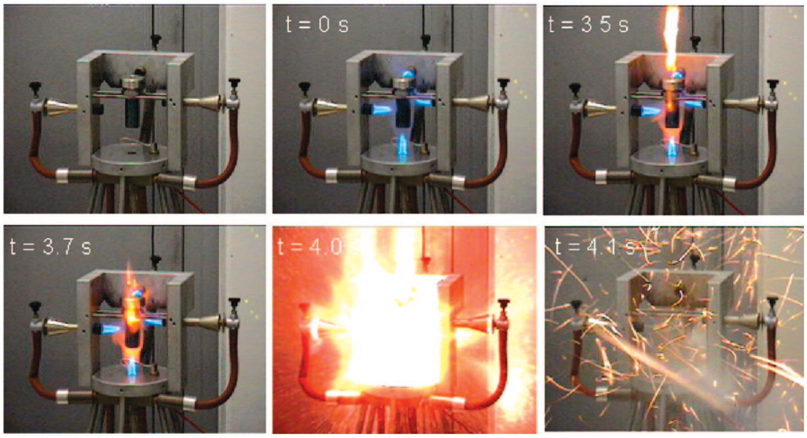

**Figure 6.** Steel sleeve (Koenen) test on 15 g of **HBT** (hole diameter: 8 mm). The pictures were taken at ignition (*t* = 0 s), 3.5 s after ignition, 3.7 s after ignition, 4 s after ignition (detonation), and 4.4 s after ignition.

**Table 5. Fragmentation Degree for the Koenen (Steel-Sleeve) Test**

| types of fragments | description | result |
|---|---|---|
| 0 | thimble is unchanged | |
| A | thimble plate is dented in | |
| B | thimble plate and sides are dented in | |
| C | thimble plate is broken | |
| D | thimble is teared up | |
| E | thimble is put in two parts | |
| F | thimble is destroyed in three or more big pieces, which can be connected | explosion |
| G | thimble is destroyed into little pieces, top is undamaged | explosion |
| H | thimble is damaged in a lot of little pieces, the top is damaged too | explosion |

tially be achieved. According to Table 5, which shows a classification of the types of fragments that result after a steel-sleeve test, **HBT** can be classified as forming type G fragments, whereas **$G_2ZT$** explodes giving type F fragments (potentially type G, considering a complete explosion).

## Long-Term Stability and Thermal Shock

The long-term thermal stabilities of **HBT** and **$G_2ZT$** were measured by thermal safety calorimetry using a Systag FlexyTSC instrument[47] in combination with a RADEX V5 oven and the SysGraph software. The samples to be measured (~300 mg) were loaded in a glass test-vessel and the tests were conducted at atmospheric pressure at a temperature of ~40 °C below the decomposition temperature of the compound in question for a period of 48 h. In addition to the pure compounds, homogeneous mixtures of the same with copper powder were also tested in order to simulate the conditions in a shell-casing. The results of the experiments are shown in Figure 7. Both pure compounds are thermally stable over the measurements, which translates in storages periods of over 50 years at room temperature. As for the mixtures with copper powder, **HBT** shows some decomposition after heating at 170 °C for 6 h but the color of the sample before and after the 48 h remains the same, which indicates that the decomposition is minor. On the other hand, **$G_2ZT$**/Cu mixtures show no sign of decomposition from the TSC plots or by comparing the color of the samples before and after the test. Hence, we conclude that both pure compounds show good long-term stabilities at high temperatures, which is the basic requirement for possible applications. Apart from some minor decomposition for **HBT**/Cu, the shell-casing simulation samples show reasonable long-term stability as well.

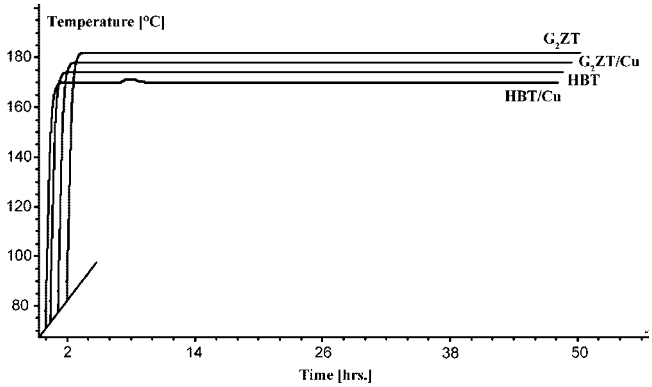

**Figure 7.** Radex plot for the long-term thermal stability of **HBT** and **$G_2ZT$** and mixtures with copper (Cu).

**Table 6. Response to Thermal Shock of HBT and $G_2ZT$ and Mxtures with AN and ADN**[a]

| | neat (powder) | neat (pellet) | +AN[b] | +ADN[b] |
|---|---|---|---|---|
| HBT | deflagrates (s) | deflagrates (s) | s (1:3) | s (1:2) |
| $G_2ZT$ | deflagrates (n.s.) | burns (n.s.) | s (1:4) | s (1:3) |

[a] s and n.s. = smokeless and nonsmokeless combustion, respectively. [b] The compound:AN and compound:ADN mixture ratios are given in parentheses.

The responses to thermal shock of **HBT**, **$G_2ZT$**, and their mixtures with ammonium nitrate (AN) and ammonium dinitramide (ADN) in an approximately neutral oxygen balance were assessed by putting the compounds in contact with a flame (Table 6). Both neat powders deflagrated, **HBT** giving a bright yellow flame with no smoke and **$G_2ZT$** forming little smoke (Figure 7). When the compound was pressed into a pellet and held into a flame, **HBT** deflagrated rapidly with almost no smoke, whereas **$G_2ZT$** burned much more slowly, producing a dense smoke. The mixtures of both compounds with an oxidizer (AN or ADN) burned smokeless in all four cases, much faster when using **HBT** and ADN as the oxidizer. In all four cases, the source of heat needs to be continuously applied for complete combustion, and for **HBT/**

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(47) http://www.systag.ch.

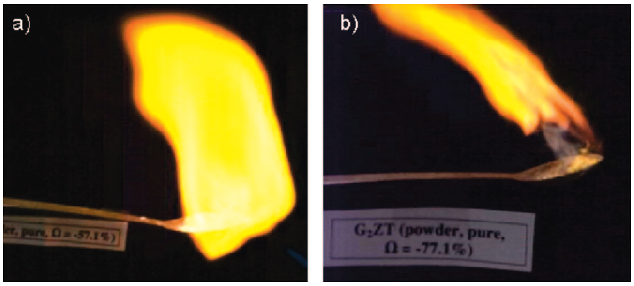

**Figure 8.** Combustion of (a) **HBT**, smokeless, and (b) **$G_2ZT$**, nonsmokeless, powders.

ADN mixtures, the amount of gas released is so large that the flame extinguishes itself.

## Decomposition Experiments

Figure 9 shows the IR spectra of the decomposition gases for **HBT** and **$G_2ZT$**. In both cases only $NH_3$ and HCN could be detected. The formation of both gases was corroborated by mass spectrometry (MS, Figure 10), as reported in the experimental part. Because of its lack of a dipole moment, molecular nitrogen could not be detected by IR but MS measurements showed it to be the major decomposition gas, as expected from the high nitrogen content of both compounds. In addition, trace amounts of hydrazine were detected in the MS decomposition experiments of **$G_2ZT$** (obscured in the IR spectrum).

The ICT computer code[48] was used to predict the decomposition gases (Figure 10). Nitrogen was estimated to be the major decomposition product. Small amounts of hydrogen and methane were expected, the first was not observed experimentally because of the range in which the spectra were recorded and the second was detected neither by the IR nor MS experiments.

From the values presented above, it would seem that the bistetrazoles studied here decompose to form mainly $N_2$ but also considerable amounts of highly toxic HCN.

Loebecke et al.[49] explained that the decomposition of the 5,5′-azotetrazolate anion proceeds via the protonated species and subsequent ring-opening, either to form hydrazoic acid, $(CN)_2$, and nitrogen or, as shown in Figure 11, to form cyanuric acid and nitrogen via a nitrilimine intermediate. Because of the absence of $HN_3$ in both the IR and the mass spectra, it is suggested that the latter is a most plausible mechanism for the decomposition of the anion in **$G_2ZT$**.

## Conclusions

A method for the synthesis of 5,5′-hydrazinebistetrazole (**HBT**) and bis(3,4,5-triamino-1,2,4-triazolium) 5,5′-azotetrazolate (**$G_2ZT$**) has been introduced that allows us to obtain both materials on a multigram scale. The extensive hydrogen bonding in the crystal structure of both compounds has been described by means of graph-set analysis and accounts for the relatively high densities of both materials (**HBT**, $\rho = 1.841\ g\ cm^{-3}$; **$G_2ZT$**, $\rho = 1.708\ g\ cm^{-3}$), which are, in turn, reflected in their performances and high stabilities. Bomb calorimetry measurements allowed us to determine their energies of formation, which were used to calculate the detonation parameters using the EXPLO5-code. **HBT** has a high performance comparable to that of some of the best high-performing known materials such as HMX or CL-20, whereas **$G_2ZT$** has calculated detonation parameters similar to those of RDX. However, both compounds are (in general) much less sensitive to classical stimuli than commonly used energetic materials making them safer for transport and use. Lastly, both **HBT** (specially) and **$G_2ZT$** meet nearly all of the criteria for new energetic materials, making them of interest for future study or as prospective energetic materials to be used as solid propellants or in propellant charges.

## Experimental Section

***Caution!*** *Although no problems occurred during the synthesis and handling of the materials studied in this work, tetrazoles are HEDMs and tend to explode under certain conditions. Laboratories and personnel should be properly grounded and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast screens are necessary, in particular when working on the larger scales described in this paper.*

**General Method.** All chemicals and solvents (analytical grade) were used as supplied by Sigma-Aldrich Inc. The chemical shifts are given relative to tetramethylsilane as external standard. Elemental analyses were performed with a Netsch Simultanous Thermal Analyzer STA 429. Melting points were determined using a Büchi B-540 apparatus and are uncorrected. $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO-$d_6$ at or near 25 °C.

**Decomposition Experiments.** A steel bomb (predried in the oven at 100 °C for several days) was loaded with the corresponding bistetrazole (~120 mg). One end of the bomb was sealed and the other end was attached to a valve for gas transfer after the explosion had occurred. Using a high vacuum pump ($\sim 1 \times 10^{-3}$ mbar), the bomb was evacuated and the valve closed. The explosion and/or decomposition was induced by heating the end of the bomb containing the product for several minutes until a small explosion was heard. The decomposition gases were allowed to expand in the bomb and diffuse into a mass spectrometer (JEOL MStation JMS 700).[50] The reservoir of the spectrometer had been evacuated during 15 min prior to opening the valve in the bomb. The explosion gases were then analyzed by mass spectrometry using electron impact ($EI^+$) mode (mass range 8–120, 1 scan per second). For the IR measurements, the same bomb was attached to a previously evacuated IR gas cell (NaCl windows) and the gases were left to slowly diffuse into it. The IR spectra of the samples were recorded (5 scans, 4000–450 $cm^{-1}$, resolution = 4.0) on a Perkin-Elmer Spektrum One FT-IR instrument.[51]

**Bomb Calorimetry.** For the calorimetric measurements, a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 207A oxygen bomb for the combustion of highly energetic materials was used.[52] A Parr 1755 printer, furnished with the Parr 1356 calorimeter, was used to produce a permanent record of all activities within the calorimeter. The samples (~200 mg each) were carefully

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(48) (a) ICT-Thermodynamic Code, version 1.0; Fraunhofer-Institut für Chemische Technologie (ICT): Pfinztal, Germany 1988–2000. (b) Webb, R.; van Rooijen, M. *Proceedings of the 29th International Pyrotechnics Seminar*, Westminster, Colorado, July 14−19, 2002; International Pyrotechnics Society: Fort Collins, CO, 2002; pp 823–828. (c) Bathelt, H.; Volk, F. In *27th International Annual Conference of ICT*; Fraunhofer Institut Chemische Technologie: Pfinztal, Germany, 1996; Vol. 92, pp 1–16.

(49) Loebecke, A.; Pfeil, A.; Krause, H.; Sauer, J.; Holland, U. *Propell. Explos. Pyrotech.* **1999**, *24*, 168–174.

(50) http://www.jeol.co.kr.

(51) http://www.perkinelmer.com.

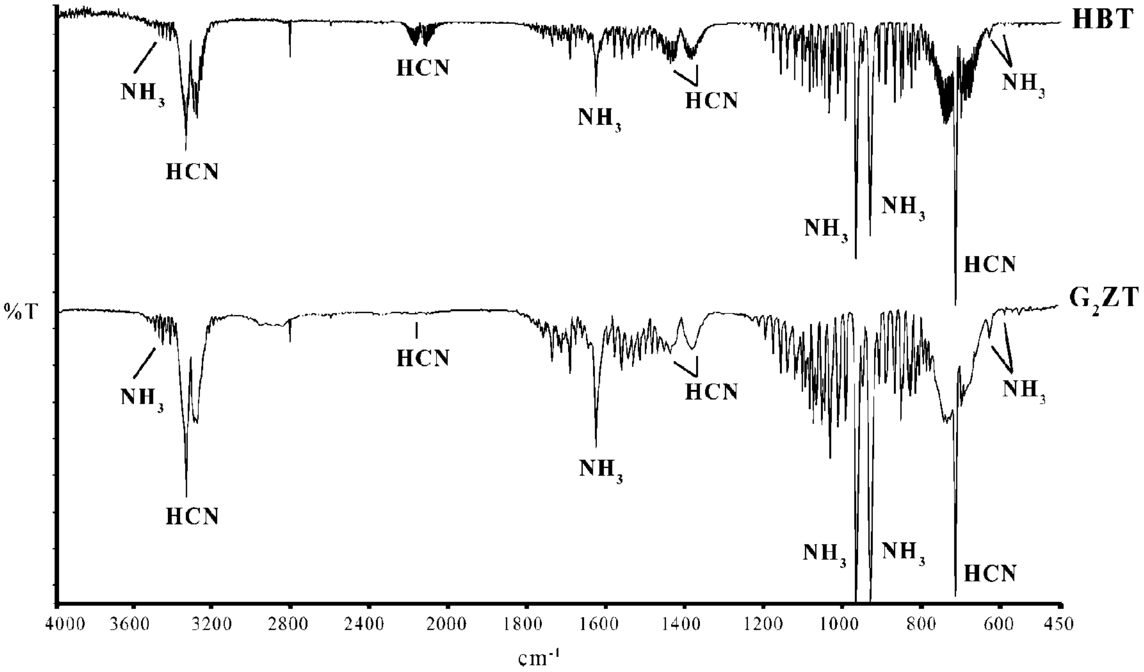

**Figure 9.** IR spectra of the decomposition gases of **HBT** (top) and **$G_2ZT$** (bottom).

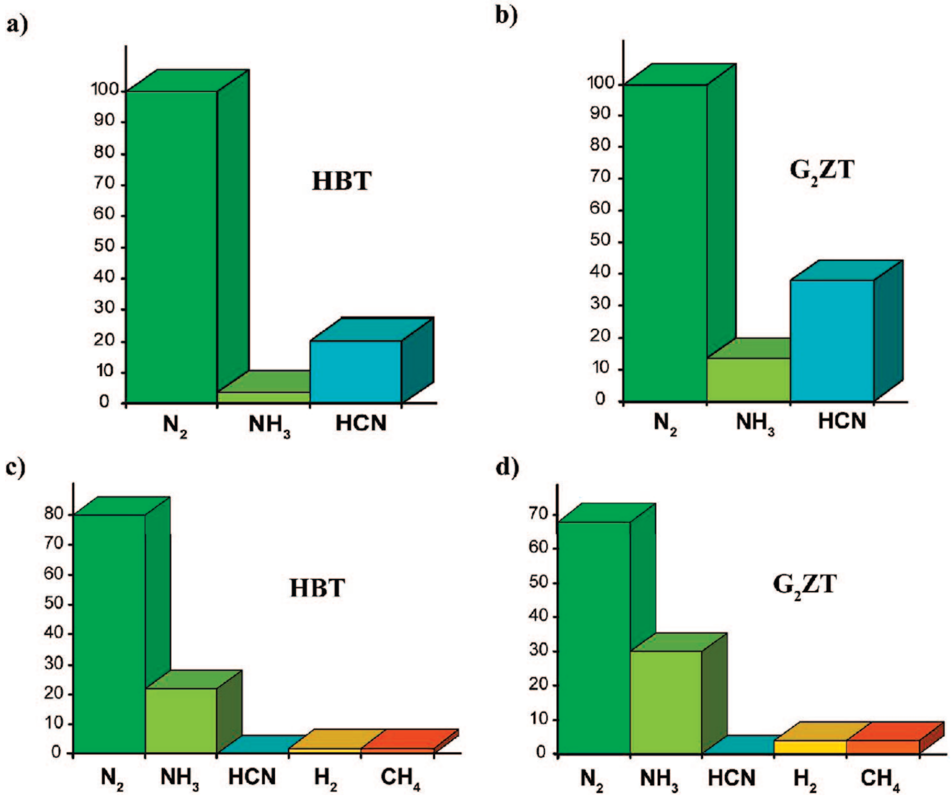

**Figure 10.** Molar percentages of the decomposition gases of **HBT** and **$G_2ZT$**: experimental using MS (top, normalized) and calculated using the ICT computer-code (bottom). The experimental percentages of HCN in (a) and (b) are highly overestimated because of the ease of ionization of the same.

mixed with ~800 mg analytical grade benzoic acid and pressed into pellets, which were subsequently burned in a 3.05 MPa atmosphere of pure oxygen. The experimentally determined heats of combustion were obtained as the averages of three single measurements.

**Synthesis of 5,5′-Hydrazinebistetrazole (HBT).** Sodium 5,5′-azotetrazolate pentahydrate (50.00 g, 166.63 mmol) was dissolved in 1.4 L of water before an excess of magnesium powder (28.71 g, 1.18 mol) was added to the yellow solution. The reaction mixture was refluxed for 6 h and left to cool to room temperature under a stream of nitrogen. The excess magnesium powder was filtered along with some magnesium hydroxide, which precipitated on cooling (this operation has to be carried out quickly in order to prevent oxidation of sodium 5,5′-hydrazinobistetrazolate) into a

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(52) http://www.parrinst.com.

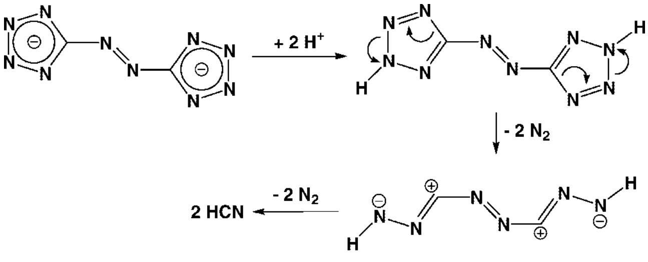

**Figure 11.** Decomposition mechanism that leads to the formation of HCN, as suggested by Loebecke et al.[47]

sidearm flask containing 160 (1.58 mol) mL of 6 M HCl (once the filtrate came into contact with the HCl no oxidation of the hydrazino-bridged compound was observed). A white solid immediately formed and the sidearm flask was shaken thoroughly to favor the precipitation of the product. The slightly yellow powder was filtered off and washed thoroughly with water and with acetone, yielding the desired product as a white powder (26.64 g, 95.2%). Crystals of the compound suitable for structure determination were grown by dissolving a small amount of the solid in boiling water and letting to cool slowly. $C_2H_4N_{10}$ (calcd/found, %): C, 14.29/14.27; H, 2.40/2.58; N, 83.31/82.68. Mp (Büchi B-540, uncorrected): 206.9–208.2 °C (decomposition). $^1$H NMR (DMSO-$d_6$, 400.18 MHz, 25 °C, TMS): $\delta$ 9.66 (4H, s, NH). $^{13}$C{$^1$H} NMR (DMSO-$d_6$, 100.63 MHz, 25 °C, TMS): $\delta$ 159.68 (s, $CN_3$); **Decomposition Experiments.** MS (EI): $m/z$ = 12 (0.1, $C^+$), 14 (0.6, $N^+$), 16 (1.2, $NH_2^+$), 17 (3.6, $NH_3^{\cdot +}$), 26 (3.2, $CN^+$), 27 (20.4, $HCN^{\cdot +}$) and 28 (100.0, $N_2^{\cdot +}$). IR (Gas): $\Delta\nu$ (cm$^{-1}$) 3332 (w, $NH_3$), 3336 (s, HCN), 3282 (s, HCN), 2168 (w, HCN), 2102 (w, HCN), 1621 (m, $NH_3$), 1431 (w, HCN), 1380 (w, HCN), 965 (vs, $NH_3$), 926 (vs, $NH_3$), 732 (s, HCN), 710 (vs, HCN), 679 (s, HCN).

**Synthesis of Bis(3,4,5-triamino-1,2,4-triazolium) 5,5′-Azotetrazolate ($G_2ZT$).** To an aqueous solution of sodium azotetrazolate pentahydrate (31.01 g, 103.25 mmol) in 150 mL of hot water was added 3,4,5-triamino-1,2,4-triazolium bromide (40.185 g, 206.50 mmol) in 100 mL of hot water. The mixture was stirred and boiled for 3 h and the title compound, only slightly soluble in hot water, started to precipitate. After slow cooling to room temperature, the yellow solid was filtered, washed with a small amount of cold water and methanol, and air-dried (37.24 g, 91.6%). Crystals suitable for X-ray analysis were obtained by recrystallization from water of a small amount of the compound. $C_6H_{14}N_{22}$ (calcd/found, %): C, 18.28/18.22; H, 3.58/3.68; N, 78.15/77.95. Mp (Büchi B-540, uncorrected): 211.3–212.4 °C (decomposition), $^1$H NMR (DMSO-$d_6$, 400.18 MHz, 25 °C, TMS): $\delta$ 6.60 (4H, s, C-$NH_2$), 5.58 (2H, s, N-$NH_2$). $^{13}$C{$^1$H} NMR (DMSO-$d_6$, 100.63 MHz, 25 °C, TMS): $\delta$ 173.24 (2C, $[C_2N_{10}]^{2-}$), 150.31 (2C, C-$NH_2$); **Decomposition Experiments.** MS (EI): $m/z$ = 12 (0.6, $C^{4+}$), 13 (0.3, $CH^{3+}$), 14 (3.4, $CH_2^{2+}$, $N^+$), 15 (0.4, $CH_3^+$), 16 (10.0, $CH_4^{\cdot +}$, $NH_2^+$), 17 (13.6, $NH_3^{\cdot +}$), 26 (5.8, $CN^+$), 27 (38.0, $HCN^{\cdot +}$), 28 (100.0, $N_2^{\cdot +}$), 31 (0.1, $NH_2NH^+$), 32 (0.2, $NH_2NH_2^{\cdot +}$), 38 (0.0, $CCN^{3+}$), 39 (0.0, $CHCN^{2+}$), 40 (0.1, $CH_2CN^+$), 41 (0.2, $CH_3CN^{\cdot +}$). IR (Gas): $\Delta\nu$ (cm$^{-1}$) 3450 (w, $NH_3$), 3333 (s, HCN), 3285 (m, HCN), 2166 (w, HCN), 2102 (w, HCN), 1623 (s, $NH_3$), 1431 (w, HCN), 1382 (w, HCN), 964 (vs, $NH_3$), 925 (vs, $NH_3$), 731 (m, HCN), 714 (vs, HCN), 681 (m, HCN), 667 (w, $NH_3$), 624 (vw, $NH_3$).

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