

Article

Preparation, Crystal and Properties of Nitrogen-Rich Energetic Salt of Bis(semicarbazide) 5,5'-Bitetrazole-1,1'-diolate

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Academic Editor: Gerhard Laus

Received: 26 December 2015; Accepted: 3 February 2016; Published: 6 February 2016

Abstract: A novel energetic salt of Bis(semicarbazide) 5,5'-bitetrazole-1,1'-diolate [2(SCZ)·BTO] was synthesized by using semicarbazide hydrochloride and 1*H*,1'*H*-5,5'-bitetrazole-1,1'-diol (BTO) as raw materials, and its structure was characterized by elemental analysis, Fourier Transform infrared spectroscopy (FT-IR) spectroscopy, ¹³C NMR spectrum and mass spectrum. The single crystal of the title salt was obtained and its structure was determined by an X-ray single-crystal diffractometer. Results show that 2(SCZ)·BTO belongs to the monoclinic space group *P*2₁/*c* with a density of 1.685 g·cm⁻³. The thermal decomposition behavior was investigated by differential scanning calorimetry (DSC) and thermogravimetry-derivative thermogravimetry (TG-DTG) analyses, and non-isothermal kinetic parameters were also calculated. The results indicated that it has a good thermal stability with a decomposition temperature above 200 °C. The apparent activation energies were 231.2 kJ·mol⁻¹ (Kissinger's method) and 228.1 kJ·mol⁻¹ (Ozawa-Doyle's method), respectively, and the critical temperature of thermal explosion is 240.6 °C. The enthalpy of formation for the salt was calculated as 158.1 kJ·mol⁻¹. The detonation pressure (*P*) and detonation velocities (*D*) of the salt were determined by using the Kamlet-Jacobs equation. The results indicated that the title salt has potential applications in the field of energetic materials.

Keywords: 1*H*,1'*H*-5,5'-bitetrazole-1,1'-diol; energetic salt; preparation; crystal structure; detonation properties

1. Introduction

There is a significant interest in the development of nitrogen-rich materials, which play an important role in the field of new energetic materials due to their potential applications as promising high-energy density materials [1–4]. Recently, much effort has been focused on the research of nitrogen-rich energetic salts with high energetic properties and low sensitivity to impact and friction [5–7]. Energetic salts, especially those with excellent performance and environmental compatibility, have been considered as aerospace propellants and explosives [8–11]. From these salts, azole heterocycles and their derivatives are a unique class due to their high heats of formation, high nitrogen contents, high densities, good thermal stabilities and environmentally benign N₂ as the main reaction product [12–14]. Their positive heat of formation is always attributed to the existence of a large number of N–N and C–N bonds, and the hydrogen bonds may also increase the density and reduce sensitivities [15,16].

Since 1*H*,1'*H*-5,5'-Bitetrazole-1,1'-diolate (BTO) was first reported by Tselinskii in 2001 [17], it has become the focal point in the energetic materials field, and the representative achievement was the synthesis of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) by Fischer and

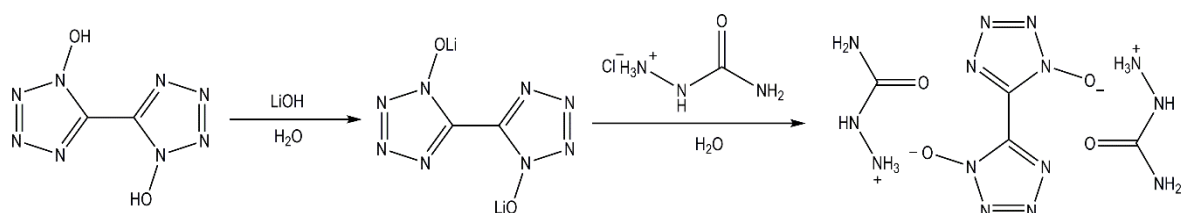
Klapötke in 2012 [18]. The nitrogen content of BTO is 65.88%, and its oxygen balance is -28.22% since introducing two hydroxyl groups in the tetrazoles, making it easy to form intra- or intermolecular bonds, which contributed to increasing the thermal and structural stability. Additionally, the hydroxyl hydrogen of BTO has a strong acid, making it easy to dissociate back into salts. Therefore, it has attracted significant attention as a good energetic anion.

In this contribution, a novel energetic salt, 2(SCZ)·BTO, based on BTO and semicarbazide (SCZ), was obtained and fully characterized. The crystal structure, thermal decomposition, and heat of combustion of the salt were investigated. In addition, its detonation properties were also determined.

2. Results and Discussion

2.1. Synthesis of the Energetic Salt 2(SCZ)·BTO

The starting material, 1*H*,1'*H*-5,5'-Bitetrazole-1,1'-diolate (BTO), was prepared according to the literature [20]. As shown in Scheme 1, the salt 2(SCZ)·BTO was synthesized by the reaction between BTO and SCZ in water with 1:2 molar quantities.



Scheme 1. Synthesis route of 2(SCZ)·BTO.

2.2. Crystal Structure

Nitrogen-rich energetic salt 2(SCZ)·BTO crystallized in the monoclinic crystal system with the space group $P2_1/c$ and a crystal density of $1.685 \text{ g}\cdot\text{cm}^{-3}$, which contained two molecules per unit cell. Further details of the structural analysis are listed in Table 1. The molecular unit and packing diagram of salt 1 are shown in Figures 1–3. Selected bond lengths and bond angles are summarized in Table 2. The hydrogen bond parameters are given in Table 3.

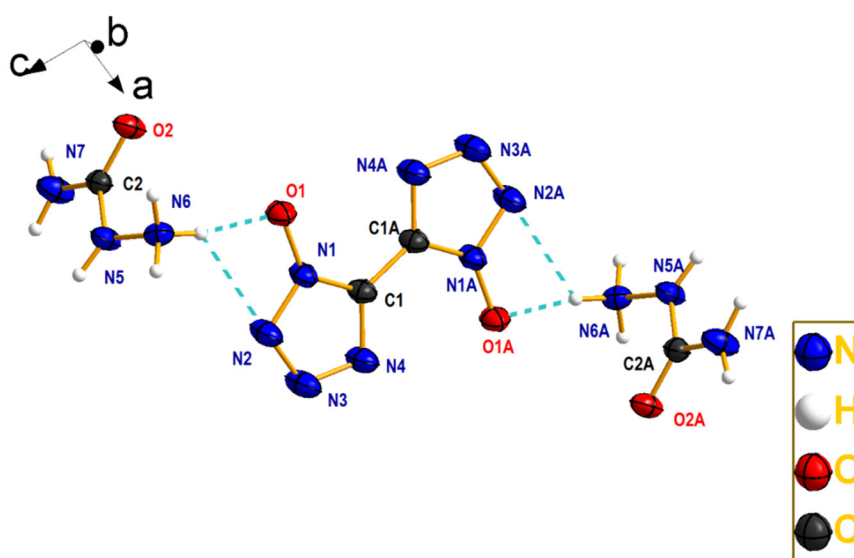
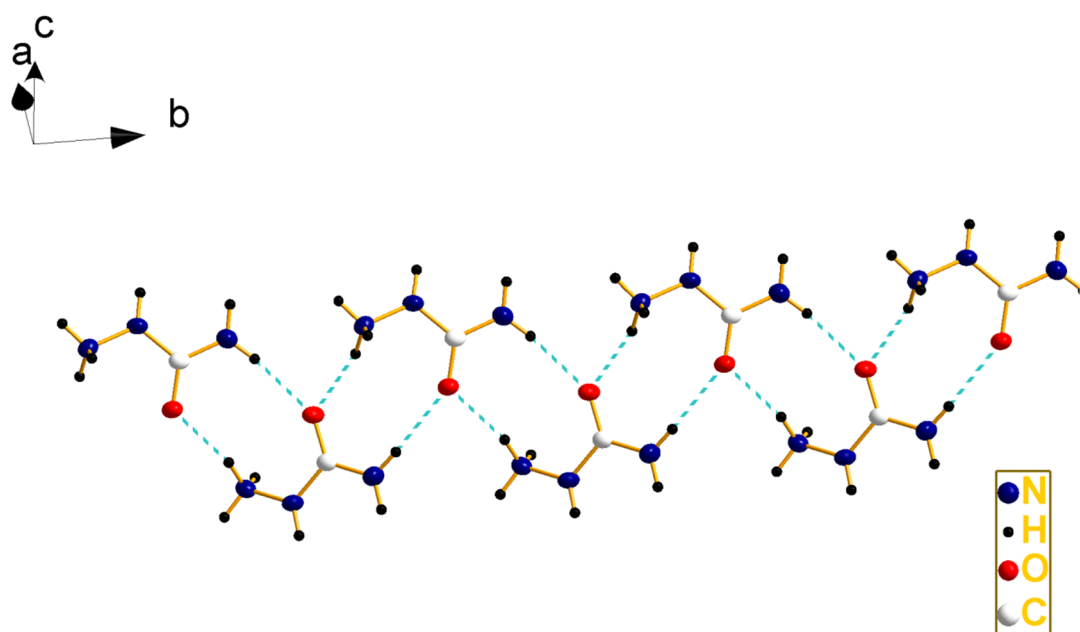


Figure 1. Molecular structure for salt 2(SCZ)·BTO. The thermal ellipsoids are drawn at the 50% probability level, the symmetry operation code is $-x + 1, -y + 1, -z + 2$.

Table 1. Crystal data and structure refinement details for salt 2(SCZ)-BTO.

Parameter	2(SCZ)-BTO
empirical formula	C ₄ H ₁₂ N ₁₄ O ₄
formula mass	320.28
temperature/K	298(2)
crystal system	monoclinic
space group	<i>P</i> 21/ <i>c</i>
<i>Z</i>	2
<i>a</i> /Å	10.2389(9)
<i>b</i> /Å	6.9576(6)
<i>c</i> /Å	8.9756(7)
β /°	99.099(2)
cell volume/Å ³	631.36(9)
<i>D_c</i> /g·cm ^{−3}	1.685
μ (Mo K α)/mm ^{−1}	0.145
<i>F</i> (000)	332
θ /°	3.55–25.02
<i>h</i> , <i>k</i> , and <i>l</i> range	−10 to 12, −8 to 8, −10 to 10
reflections collected	3023
reflections unique [<i>R</i> _{int}]	1109 [<i>R</i> _{int} = 0.0284]
data/restraint/parameter	1109/0/102
goodness-of-fit on <i>F</i> ²	1.049
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0381
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	<i>wR</i> ₂ = 0.1074 ^a
<i>R</i> ₁ (all data)	0.0448
<i>wR</i> ₂ (all data)	<i>wR</i> ₂ = 0.1147 ^a
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e·Å ^{−3})	0.453, −0.469
CCDC	1437024

Note: $w = 1/[s^2(F_o^2) + (0.0691P)^2 + 0.2637P]$, where $P = (F_o^2 + 2F_c^2)/3$.

**Figure 2.** Ribbon motif formed through hydrogen bonding between the SCZ cations in the crystal structure.

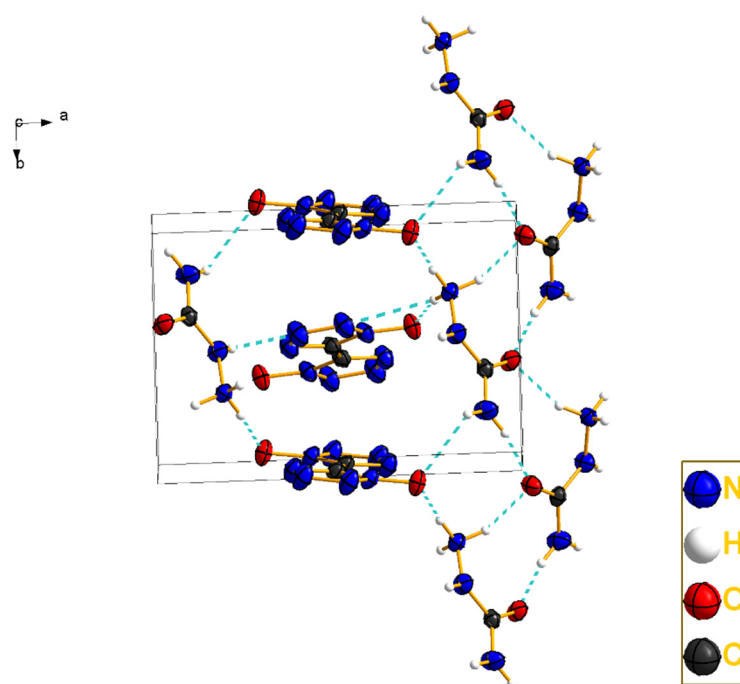


Figure 3. Packing diagram for salt 2(SCZ)·BTO.

Table 2. Selected bond lengths/Å and bond angles/° for salt 2(SCZ)·BTO.

Bond	Length	Bond	Angle
N1–O1	1.325(19)	N1–N2–O1	121.11(15)
N1–N2	1.336(2)	N1–C1–O1	129.89(15)
N1–C1	1.342(2)	N2–N1–C1	109.00(15)
N2–N3	1.315(2)	N3–N2–N1	105.53(15)
N3–N4	1.337(2)	N2–N3–N4	111.55(15)
N4–C1	1.329(2)	C1–N4–N3	105.70(16)
N5–C2	1.360(2)	C2–N5–N6	115.98(14)
N5–N6	1.421(2)	N4–C1–N1	108.21(17)
N7–C2	1.334(2)	N4–C1–C1 ^{#1}	127.30(2)
C2–O2	1.238(2)	N1–C1–C1 ^{#1}	124.50(2)
C1–C1 ^{#1}	1.446(4)	N7–C2–O2	123.09(16)
N6–O1	2.780(21)	N5–C2–O2	120.70(16)
N6–N2	3.261(24)	N7–C2–N5	116.11(16)

Note: ^{#1} $-x + 1, -y + 1, -z + 2$.

Table 3. Hydrogen bond lengths/Å and bond angles/° for salt 2(SCZ)·BTO.

D–H...A	Length(D–H)	Length(H...A)	Length(D...A)	Angle(D–H...A)
N5–H5...N3 ⁱ	0.860	2.136	2.882	144.92
N6–H6A...O2 ⁱⁱ	0.890	1.958	2.801	157.36
N6–H6B...O1 ⁱⁱⁱ	0.890	1.936	2.786	159.14
N6–H6B...N4 ^{iv}	0.890	2.481	2.997	117.39
N7–H7A...O2 ^v	0.860	2.101	2.906	155.60
N7–H7B...O1 ^{vi}	0.860	2.466	3.108	131.95
N6–H6C...O1	0.890	1.906	2.780	166.85
N6–H6C...N1	0.890	2.594	3.438	158.53
N6–H6C...N2	0.890	2.621	3.261	129.52

Note: ⁱ $-x + 1, -y + 1, -z + 1$; ⁱⁱ $-x + 2, y - 1/2, -z + 3/2$; ⁱⁱⁱ $x, -y + 1/2, z - 1/2$; ^{iv} $-x + 1, y - 1/2, -z + 3/2$; ^v $-x + 2, y + 1/2, -z + 3/2$; ^{vi} $x, -y + 3/2, z - 1/2$.

As shown in Figure 1, the energetic salt 2(SCZ)·BTO can be presented as the form of $(\text{CH}_6\text{N}_3\text{O})_2^+(\text{C}_2\text{N}_8\text{O}_2)^{2-}$, which is composed of two SCZ cations and a BTO anion which is formed by the combination of ionic bonds and hydrogen bonds. The two hydroxyl H atoms of BTO are lost in the reaction, forming a negative bivalence anion. While, for SCZ hydrochloride, the electronegativity of the N5 atom in the hydrazine group was higher than that of the C2 atom, the ability to attract protons for N6 was increased, which led to the transfer of the proton from BTO to the N6 position, and then formed the type of $-\text{NH}_3^+$ cation. Finally, the SCZ cations and BTO anion formed a stable structure of salt 2(SCZ)·BTO by electrostatic force and hydrogen bonds such as $\text{N6}-\text{H}\cdots\text{O1}$ and $\text{N6}-\text{H}\cdots\text{N2}$.

As shown in Table 2, in the BTO anion, the N–N bond lengths range from 1.315 Å for N2–N3 to 1.337 Å for N3–N4 with an average value of 1.329 Å, which was 0.125 Å shorter than the normal N–N bond length (1.454 Å) and 0.084 Å longer than the normal N=N bond (1.245 Å) [19]. The C–N bonds were 1.329 Å for N4–C1 and 1.342 Å for N1–C1, shorter than the normal C–N bond of 1.47 Å and longer than the normal C=N bond of 1.27 Å [19], while the C–C bond was 1.446 Å, which is in the normal range of 1.32 Å for the C=C bond and 1.53 Å for the C–C bond. The bond angles for the tetrazole ring of the BTO anion have a max of 129.89° for N1–C1–O1 and 105.53° for N3–N2–C1. The dihedral angle for N1–C1–C1A–N1A is -180.00° , and for N4–C1–C1A–N4A it is also -180.00° , which indicated the two pentagons in the BTO are coplanar in the salt. Some multiple-bond character was present, which indicated that the tetrazole ring existed as a large π -conjugated system. Additionally, it was an irregular pentagon, due to the presence of oxygen atoms [20].

The hydrogen bond is an important factor in stabilizing the crystal structure for the title salt. In this crystal, the SCZ cations are interconnected through hydrogen bonds with each other, which formed a ladder-like ribbon motif, as can be seen in Figure 2. A more detailed description for how the layers are formed not only between BTO anions and SCZ cations but also between SCZ cations through the different N–H $\cdots$ O hydrogen bonds from the hydroxyl and amino groups, as well as a number of C=O bonds, is shown in Figure 3. The N6 atoms from the cations and O1 as well as N2 atoms from the anions are engaged in the N–H $\cdots$ O and N–H $\cdots$ N hydrogen bonds, which connected the SCZ^+ and BTO^{2-} tightly. At the same time, the amidinium hydrogen of the cationic SCZ moiety also forms a N–H $\cdots$ O hydrogen bond to a carbonyl oxygen atom of the neighboring cations. Additionally, the ribbon motifs are cross-linked by the BTO anions, which formed a structure similar to the steps on a ladder.

Details of the hydrogen bonding in the structure of the salt are summarized in Table 3. The strong intermolecular hydrogen bond between the nitrogen-rich cation and bi-tetrazole anion may make an important contribution in enhancing the thermal stability and decreasing the sensitivity of the salt.

2.3. Thermal Decomposition and Non-Isothermal Kinetic Analysis

The DSC and TG-DTG measurements were applied to investigate the thermal behavior of the salt. The DSC and TG-DTG curves at a linear heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$, recorded in a nitrogen atmosphere, are given in Figures 4 and 5.

There was only one exothermic process on the DSC curve for salt 2(SCZ)·BTO: it decomposed at 239.9°C before melting, and the peak temperature was 245.3°C . The enthalpy of this exothermic process was $96.4\text{ kJ}\cdot\text{mol}^{-1}$. Correspondingly, there was a main mass loss stage in the TG-DTG curve as well. It occurred from 201.6°C to 252.3°C with a mass loss of 57.6%, in which the largest mass rate was reached at 241.8°C . This process showed the main exothermic decomposition of the salt. The final stage was a slow process of thermal decomposition with continuous mass loss with a final residue mass of 17%. After the decomposition process the products of the salt were H_2O , CO_2 , N_2 and a small amount of residue.

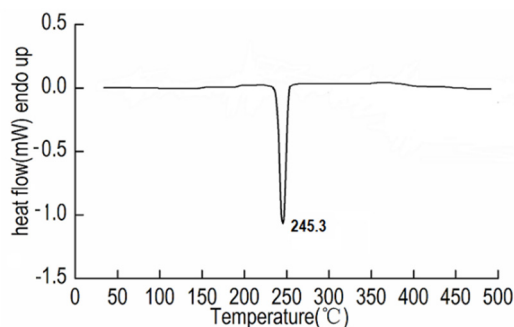


Figure 4. DSC curve of 2(SCZ)·BTO at the heating rate of 5 °C·min^{−1}.

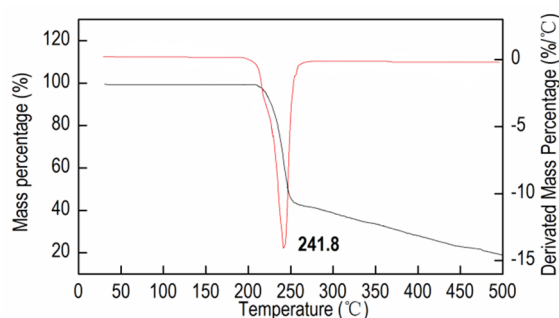


Figure 5. TG-DTG curve of 2(SCZ)·BTO at the heating rate of 5 °C·min^{−1}.

Kissinger's method [21] and Ozawa-Doyle's method [22] are widely used to study the kinetic parameters of the rapidly exothermic process of the title salt, based on the DSC curves obtained under different heating rates. The Kissinger and Ozawa-Doyle equations are as follows:

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{A_k R}{E_k}\right) - \frac{E_k}{R} \frac{1}{T_p} \quad (1)$$

$$\log\beta + \frac{0.4567E_a}{RT_p} = C \quad (2)$$

where T_p is the peak temperature, °C; R is the gas constant, 8.314 J·mol^{−1}·°C^{−1}; β is the linear heating rate, °C·min^{−1}; and C is a constant.

On the basis of the peak temperatures (T_p) of the first exothermic process occurring in the DSC curves under four different heating rates (5, 10, 15 and 20 °C·min^{−1}) of the salt, the apparent activation energy E_k and E_o , pre-exponential factor A_k , and linear coefficient R_k and R_o were determined and listed in Table 4. The calculated results using both methods correspond well with each other, and they are all in the normal range of kinetic parameters for the thermal decomposition of solid materials [23]. Accordingly, the Arrhenius equation of the salt can be expressed as follows (E is the average of E_k and E_o): $\ln k = 21.21 - 229.65 \times 10^3/RT$.

Table 4. Peak temperatures and non-isothermal kinetic parameters of 2(SCZ)·BTO.

Heating rates (°C·min ^{−1})	5	10	15	20
Peak temperatures T_p (°C)	245.3	252.7	256.1	258.4
Kissinger's Method		Ozawa's Method		
E_k (kJ·mol ^{−1})	$\lg[A_k(s^{-1})]$	R_k	E_o (kJ·mol ^{−1})	R_o
231.2	21.21	−0.9968	228.1	−0.9970

Note: E is the apparent activation energy. A is the pre-exponential factor. R is the linear correlation coefficient. The subscript k and o represent Kissinger's method and Ozawa's method, respectively.

2.4. Calculation of the Thermal Explosion Properties and Enthalpy of Formation

The thermal explosion critical temperature (T_{bp}) is widely used to evaluate the thermal safety of energetic materials. The value of the peak temperature corresponding to $\beta \rightarrow 0$ (T_{p0}) was obtained as 231.0 °C, according to Equation (3), where a , b , and c are coefficients [24].

$$T_{pi} = T_{p0} + a\beta + b\beta^2 + c\beta^3 \quad (3)$$

The corresponding critical temperature of the thermal explosion (T_{bp}) was calculated by Equation (4), where R is the gas constant, E is the value of E_k by Kissinger's method [24]. The value was 240.6 °C, respectively.

$$T_{bp} = \frac{E - \sqrt{E^2 - 4ERT_{p0}}}{2R} \quad (4)$$

The entropy of activation ($\Delta S^\ddagger$), enthalpy of activation ($\Delta H^\ddagger$), and free energy of activation ($\Delta G^\ddagger$) of the decomposition reaction corresponding to $T = T_{p0}$ and $A = A_k$ (from Kissinger's method) obtained by Equations (5)–(7) are as follows:

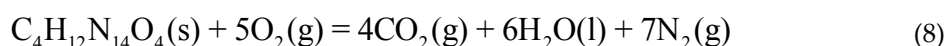
$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} \quad (5)$$

$$\Delta H^\ddagger = E - RT \quad (6)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (7)$$

where k_B is the Boltzmann constant, 1.381×10^{-23} J·K⁻¹, and h is the Planck constant, 6.626×10^{-34} J·s. The calculated values are as follows: $\Delta S^\ddagger = -72.94$ J·K⁻¹·mol⁻¹; $\Delta H^\ddagger = 227.01$ kJ·mol⁻¹; $\Delta G^\ddagger = 263.78$ kJ·mol⁻¹.

The heat of combustion and enthalpy of formation are significant characteristics for accessing the energetic properties of a new compound. The constant-volume combustion heat (Q_v) of the salt was -10.8084 MJ·kg⁻¹, respectively, as measured by Parr 1104 oxygen bomb calorimetry in an oxygen atmosphere (450 psi). The bomb equation and the heat of combustion equation are as follows (Q_p is the constant-pressure energy of combustion, accurate to 0.001):



$$\Delta H = Q_p = Q_v + \Delta nRT \quad (9)$$

The value of Q_p was -3446.8306 kJ·mol⁻¹. Additionally, the standard enthalpy of the formation of the salt was calculated on the basis of Equations (8) and (9). With the known enthalpies of formation of the carbon dioxide, $\Delta_f H_{298}^\circ[CO_2(g)] = -393.5$ kJ·mol⁻¹, and water, $\Delta_f H_{298}^\circ[H_2O(l)] = -285.8$ kJ·mol⁻¹, the enthalpy of formation of the salt can be calculated as 158.1 kJ·mol⁻¹ [25].

$$\Delta_f H_{298}^\circ[2(SCZ \cdot BTO)] = 6\Delta_f H^\circ(H_2O, l) + 4\Delta_f H^\circ(CO_2, g) - \Delta_c H^\circ(s) \quad (10)$$

2.5. Detonation Parameters

The critical detonation parameters of energetic compounds including the detonation velocity (D) and pressure (P) were predicted by Empirical Kamlet-Jacobs equations [26]:

$$D = 1.01(NM^{0.5}Q^{0.5})^{0.5}(1 + 1.30p) \quad (11)$$

$$P = 1.558\rho^2 NM^{0.5}Q^{0.5} \quad (12)$$

where D is the detonation velocity (km·s⁻¹); P is the detonation pressure (GPa); N is the moles of detonation gases per gram of explosive; M is the average molecular weight of these gases; Q is the heat of detonation (kJ·kg⁻¹); ρ is the loaded density of explosives (g·cm⁻³).

With the value for the enthalpy of formation and density of the title energetic salt, the critical detonation parameters P and D were determined as 23.5 GPa and 7433.9 m·s⁻¹, which were better than those of trinitrotoluene (TNT, 19.5 GPa and 6881 m·s⁻¹) and lower than those of cyclotrimethylenetrinitramine (RDX, 34.9 GPa and 8748 m·s⁻¹), respectively [27].

3. Materials and Methods

3.1. Materials and Physical Techniques

All chemicals used reagents and solvents were analytically pure, and purchased commercially. Elemental analysis was performed on a flash EA 1112 full automatic trace element analyzer (Thermo Electron SPA, Waltham, MA, USA). The IR spectra were recorded with a Nexus-470 FT-IR (Nicolet, Madison, WI, USA) spectrometer using KBr pellet in the range of 4000 to 400 cm⁻¹ with the resolution of 6 cm⁻¹. The DSC and TG measurements were carried out by using a Pyris-1 differential scanning calorimeter and a Pyris-1 thermogravimetric analyzer (Perkin Elmer, Waltham, MA, USA) under dry nitrogen atmosphere with flowing rate of 20 mL·min⁻¹. The energy of combustion was determined by a Parr 6200 oxygen bomb calorimeter (Parr, Moline, IL, USA) with a sample of 500 mg.

3.2. Synthesis of the Energetic Salt 2(SCZ)·BTO

The 1H,1'H-5,5'-Bitetrazole-1,1'-diolate dihydrate (0.206 g, 1 mmol) was suspended in a few milliliters of water. LiOH (0.084 g, 2 mmol) was added slowly to the clear solution. The mixture was filtered after stirring in room temperature for 10 min. Then the colorless solution was heated to boiling after adding semicarbazide hydrochloride (0.223 g, 2 mmol) for half an hour. The solution was cooled to room temperature, and the colorless crystalline residue was filtered, 0.263 g (82% yield) was obtained. ¹³C NMR(DMSO-*d*₆, 100 MHz, δ): 159.91, 135.55. IR (KBr, ν /cm⁻¹): 3415, 3185, 2656, 2042, 1695, 1596, 1528, 1399, 1222, 1171, 1140, 1046, 999, 931, 731, 645, 482. MS(ESI⁻), m/z : 84.0 [CN₄O⁻]. Anal. calcd for C₄H₁₂N₁₄O₄ (320.28): C 15.00, H 3.78, N 61.24; found C 14.87, H 3.81, N 61.32.

3.3. X-Ray Single-Crystal Determination

A Bruker CCD area-detector diffractometer (Bruker, Karlsruhe, Germany) using graphite-monochromated Mo K α radiation (λ = 0.071073 nm) was applied for structure analyses of the target salt SCZ·BTO. Single crystal suitable for X-ray measurement was obtained by slow evaporation of solution, and a colorless crystal with dimensions of 0.45 × 0.40 × 0.28 mm was chosen for X-ray determination. The data were collected using π and σ scan modes at 298 K, and the range was from 3.55° to 25.02°. The structures were solved by direct methods using SHELXS-97 [28] and refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 programs [29]. All non-hydrogen atoms were found directly from the differential Fourier map, and the hydrogen atoms were added according to theoretical models.

4. Conclusions

A novel nitrogen-rich energetic salt of 1H,1'H-5,5'-bitetrazole-1,1'-diol and semicarbazide was synthesized with a ratio of 1:2 in water solution, and the title salt was fully characterized by single-crystal X-ray diffraction. The DSC and TG-DTG analysis indicate that the salt decomposed at 239.9 °C, with the peak temperature of 245.3 °C, and the critical temperature of thermal explosion is 240.6 °C. The results indicated that the salt has a good thermal stability. Non-isothermal kinetic analysis showed that the Arrhenius equation of the salt can be expressed as follows: $\ln k = 21.21 - 229.65 \times 10^3/RT$. The enthalpy of formation of the salt was determined as 158.1 kJ·mol⁻¹. The detonation pressure (P) and detonation velocities (D) of the salt were determined by using the Kamlet-Jacobs equation as 23.5 GPa and 7433.9 m·s⁻¹, respectively.

Based on the good thermal stability and relatively good detonation properties, the title salt 2(SCZ)·BTO might have a promising future in applications as an environmentally friendly energetic material.

Acknowledgments: It should be gratefully acknowledge the financial support from the National Natural Science Foundation of China, and the project of State Key Laboratory of Science and Technology (ZDKT 12-03 & YBKT16-04).

Author Contributions: Z.-B. Zhang conceived, designed and performed the experiments; Z.-B. Zhang and L. Yin analyzed the data; X. Yin contributed analysis tools; and Z.-B. Zhang wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

The following abbreviations are used in this manuscript:

Abbreviations	Definition
SCZ	semicarbazide
BTO	1H,1'H-5,5'-bitetrazole-1,1'-diol
FT-IR	Fourier Transform infrared spectroscopy
DSC	Differential ScanningCalorimetry
TG-DTG	Thermogravimetric differential heat
$\Delta S^\#$	The entropy of activation
$\Delta H^\#$	The enthalpy of activation
$\Delta G^\#$	The free energy of activation
P	detonation pressure
D	detonation velocities

Appendix B

CCDC-1437024 contained the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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