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An unusual layered crystal packing gives rise to a superior thermal stability of energetic salt of 3,6-bishydrazino-1,2,4,5-tetrazine

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Abstract: Five energetic salts of 3,6-Bishydrazino-1,2,4,5-tetrazine (BHT) were synthesized and fully characterized by elemental analysis, FT-IR and mass spectra. They are $(BHT)_2(NTO)_3$ (**3**), $(BHT)(BTT)\cdot 2H_2O$ (**4**), $(BHT)(DNP)_2$ (**5**), $(BHT)(NATr)_2$ (**6**), $(BHT)(FOX-7)_2$ (**7**), respectively. Of which two crystal structures **3** and **4** were obtained and determined. Sensitivities towards outside stimuli and thermal behaviors of all the compounds were investigated, besides, thermodynamics of both **3** and **4** were calculated as well. All the compounds exhibit splendid thermal stabilities and satisfactory sensitivities simultaneously. Notably, unlike the previously known layered packing, compound **4** was found to adopt an unusual layered crystal packing with arch layers alternately arranged upward or downward. It may play an important role in contributing to its superior thermal stability (350 °C), providing an enlightening thinking to design new highly thermal stable energetic materials.

Introduction

Energetic materials include explosives, propellants, and pyrotechnics that are used for a variety of military purposes and civilian applications.^[1] Recently, nitrogen-rich heterocycles are one of the high energy density materials (HEDMs) that each world power competed on, of which two important kinds are azoles and tetrazines.^[2-6] These

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high nitrogen content materials have a large number of N-N and C-N bonds and therefore exhibit large positive heats of formation. Additionally, the low percentages of C and H in these compounds have triple positive effects: (i) enhance density; (ii) allow a good oxygen balance to be achieved easily; and (iii) produce a larger number of moles of gaseous products per gram of the high-energy material.^[1] Nowadays, there is a trend that energetic ionic salts are becoming the research focus in the field of energetic materials,^[7-8] energetic ionic salts possess advantages over non-ionic molecules owing to their lower vapor pressures and higher densities. Besides, tetrazine and azole based ionic salts possess high heats of formations, the low carbon and hydrogen content rises the oxygen balance, which makes the energetic salts very promising candidates for the demands of new energetic materials.^[9]

3,6-Bishydrazino-1,2,4,5-tetrazine (BHT, **1**) was first synthesized by reacting diaminos-tetrazine with hydrazine hydrate.^[10] In 2001, a new synthetic route for BHT using 3,6bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (BT) and hydrazine hydrate heated in acetonitrile solvent was reported by *Hiskey* et al., additionally, the perchlorate and nitrate salts of BHT were also prepared by them.^[11] BHT possesses high nitrogen content (78.9%) and positive enthalpy of formation (577.0 kJ·mol⁻¹), along with its good stability and reasonable alkaline concomitantly, making it a promising cation for energetic salts.

We prepared BHT(PA)₂, BHT(HTNR)₂·H₂O and BHT(H₂TNPG)₂·2H₂O (where PA, TNR and TNPG denote trinitrophenol, trinitroresorcinol and trinitrophloroglucinol, respectively) by reacting BHT with corresponding acidic compounds directly in 2012.^[12]

In 2013, several highly energetic salts of BHT were prepared and investigated by *Klapötke* et al. These salts were obtained by reacting BHT·2HCl with freely soluble salts of corresponding acidic compounds. As a result, these salts possess relatively good properties, of which the detonation parameters of bishydrazinium-tetrazine bis (5-nitrotetrazolate) (BHT-(NT)₂) and bishydrazinium-tetrazine 4,4',5,5'-tetranitro-2,2'-bisimidazolate (BHT·TNBI) in terms of energetic applications were calculated using the EXPLO5 V5.05 computer code. According to the calculate results, both of them

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exhibit detonation performance commensurate with that of RDX, which gives rise to these energetic salts of BHT as relatively good perspectives in the area of energetic materials.^[13]

Inspired by these and in order to further explore the feasibility of BHT salts being applied as energetic materials, five brand new energetic salts of BHT were prepared, characterized and investigated by elemental analysis, FT-IR and mass spectra herein. All the compounds were directly synthesized via salt metathesis, including $(BHT)_2(NTO)_3$ (3), $(BHT)(BTT) \cdot 2H_2O$ (4), $(BHT)(DNP)_2$ (5), $(BHT)(NATr)_2$ (6) and $(BHT)(FOX-7)_2$ (7), where NTO, BTT, DNP, NATr and FOX-7 denote 3-nitro-1,2,4-triazol-5-one, 4,5-Bis(5-tetrazolyl)-1,2,3-triazole, 3,4-dinitropyrazole, 3-nitramino-1,2,4-triazole and 1,1-diamino-2,2-dinitroethylene, respectively. Among all the compounds, the crystal structures of 3 and 4 were obtained and investigated. All of them are equipped with quite reasonable thermal stabilities and insensitivities towards impact and friction. Additionally, 4 adopts an unusual layered crystal packing different from the previously reported ways, which contributes to its superior thermal stability with a decomposition temperature of 350 °C.

Results and Discussion

Synthesis

BHT was synthesized according to the previously known procedure.^[14-15] To get the utmost out of BHT in the subsequent salt metathesis, it was converted to bishydrazinium-tetrazine dichloride (1:2) (BHT-2HCl, **2**) based on literature,^[16] too, which is shown in Scheme 1.

As a result, the salt metathesis reactions proceeded smoothly by reacting BHT-2HCl with sodium salts of corresponding energetic compounds to give **3-7**. An overall synthetic protocol is displayed in Scheme 2. The specified anions were synthesized as described in the literature.^[17-20]



Scheme 1. Synthetic route of BHT-2HCl.



Scheme 2. The overall synthetic protocol of the energetic salts 3-7.

Crystal Structure

The X-ray crystallographic data were determined by using a Rigaku Saturn 724+CCD diffractometer equipped with graphite mono-chromated Mo-K_{α} radiation. The structures were solved with successive Fourier difference syntheses (with SHELXS-97) program and refined by full-matrix least squares on F2 using SHELXL-97. Crystallographic data are summarized in Table 1. Further information regarding the crystal-structure determinations have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers.

Single crystal of compound **3** (Figure 1) was obtained successfully in the anhydrous form, which crystallizes in the triclinic space group *P*-*1* with one formula unit per unit cell and a calculated density of $1.737 \text{ g} \cdot \text{cm}^{-3}$ at 293 K. The NTO anions also follow the planar structure described previously such as DATr·NTO (where DATr denotes 3,4-diamino-1,2,4-triazole),^[21] while a twisting was observed in tetrazine ring.



Figure 1. Molecular structure of **3**. Selected bond lengths (Å): C1-N2 1.341(8), C1-N3 1.331(8), C2-N1 1.331(8), C2-N4 1.353(8), C3-N10 1.339(8), C3-N11 1.351(8), C4-N9 1.304(8), C4-N12 1.420(8), C5-O1 1.296(7), C7-O4 1.267(8), C9-O7 1.300(7); selected bond angles (°): C1-N2-N1 115.7(5), C2-N1-N2 116.4(5), C1-N3-N4 115.4(5), C2-N4-N3 118.6(5), C5-N17-N18 110.6(5), C6-N18-N17 100.6(5), O1-C5-N17 124.9(5), O2-N20-O3 125.5(6); selected torsion angles (°): C5-N17-N18-C6 0.1(6), C7-N21-N22-C8 0.2(6), C9-N25-N26-C10 -0.3(6), N17-N18-C6-N20

-179.4(5), C5-N19-C6-N18 0.3(7), N25-N26-C10-N27 0.0(7).

Compound **4** (Figure 2) crystallizes in the monoclinic space group P 2(1)/c with four formula units per unit cell. The unit cell has the dimensions of a=14.4559 (12) Å, b=6.7390 (6) Å, c=16.0941 (13) Å, β =99.105 (2) °. It crystallizes with a cell volume of 1548.1 (2) Å³ and a density of 1.645 g·cm⁻³ at 298 K. It was found to have an unusual, wavelike layered crystal packing on the whole, with a pair of BHT and BTT together as the gibbous part while another pair alongside plays the concave role. Precisely speaking, both the gibbous and the concave parts are not genuinely concatenate. However, both of them adopt an arch structure, upward or downward by turns, resulting in a wavelike packing viewed as a whole, as given in Figure 3.



Figure 2. Molecular structure of **4**. Selected bond lengths (Å): N1-N2 1.329(3), N1-C2 1.341(4), N3-C3 1.341(4), C2-C3 1.407(4), C1-N4 1.320(4), C1-N7 1.326(4), C5-N12 1.340(4), C5-N15 1.378(4), C6-N13 1.315(4), C6-N14 1.369(4); selected bond angles (°): C2-N1-N2 103.0(3), N1-N2-N3 116.2(3), C4-N8-N9 104.7(3), N4-C1-N7 108.9(3), N13-C6-N14 126.9(3), N13-C6-N18 119.5(3), C6-N13-N12 117.0(3); selected torsion angles (°): C2-N1-N2-N3 0.1(4), N1-N2-N3-C3 0.7(4), C1-N4-N5-N6 -0.6(4), N4-N5-N6-N7 0.9(4), C4-N8-N9-N10 -0.4(4), N8-N9-N10-N11 0.2(4), C5-N12-N13-C6 -0.1(4), C6-N14-N15-C5 -1.8(4), N19-N18-C6-N14 164.9(3).

Compound	BHT ₂ -(NTO) ₃ (3)	BHT-BTT·2H ₂ O (4)
Formula	$C_{10}H_{21}N_{28}O_9$	$C_6H_{13}N_{19}O_2$
$FW(g \cdot mol^{-1})$	677.55	383.35
Crystal system	Triclinic	Monoclinic
Space group	Р1	P2(1)/c
Crystal size(mm)	0.15 x 0.10 x 0.06	0.35 x 0.11 x 0.05
<i>a</i> (Å)	6.8283(6)	14.4559(12)
<i>b</i> (Å)	6.9278(6)	6.7390(6)
<i>c</i> (Å)	14.3445(14)	16.0941(13)
α (°)	80.315(2)	
β(°)	76.6020(10)	
γ (°)	82.666(2)	
$V(\text{\AA}^3)$	647.90(10)	1548.1(2)
Ζ	1	4
ho (g·cm ⁻¹)	1.737	1.645
μ (mm ⁻¹)	0.150	0.133
<i>F</i> (000)	349	792
$\lambda_{MoK\alpha}(\text{\AA})$	0.71073	0.71073
<i>T</i> (K)	293(2)	298(2)
heta (°)	2.95-25.02	2.56-25.02
Reflection collected	3319	7437
Independent reflection $[R_{int}]$	2766 [$R(int) = 0.0251$]	2716 [$R(int) = 0.0730$]
$R_1, wR_2 \left[I > 2\sigma \left(I \right) \right]$	0.0508, 0.1385	0.0585, 0.1254
R_1, wR_2 (all)	0.0618, 0.1464	0.1129, 0.1404
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} \ ({\rm e} \cdot {\rm \AA}^{-3})$	0.389, -0.326	0.331, -0.301
CCDC No.	1533133	1560575

Table 1. Crystallographic data of compound 3 and 4





Figure 3. Ball-and-stick packing diagrams of compound **4** viewed down the a axis (a) and c axis (b), respectively.

In the packing diagram of both **3** and **4**, many strong interactions derived from both intermolecular and intramolecular hydrogen bonding are observed, also contributing to enhancing the stabilities.

Sensitivities and Thermal Stabilities

Values of sensitivities towards impact and friction stimuli were obtained according to BAM standard as given in Table 2. All the compounds are insensitive towards friction, even the lowest value reaches up to 240 N. Resulting from the existence of nitroamino group probably, compound **6** possesses the highest impact sensitivity (6 J). Salt **3**, **5** and **7** (12-15 J) are sensitive to impact, whereas **1**, **2** and **4** (20-30 J) are less sensitive.

Thermal stabilities of all compounds described in this work were investigated via differential scanning calorimetry(DSC). As shown in Table 2, the decomposition temperatures of all compounds range from 144 to 350 °C, exhibiting quite favorable thermal stability. Only compound **3** has an endothermic peak, maybe corresponding to the melting process. The endothermic event of water loss is absent in the DSC curve of **4**, which indicates that either water is released during the decomposition process, or crystal water is lost over the time during the storage of this material at ambient temperature. It is important to note that most of them possess thermal behavior either comparable to RDX (204 °C) or better than it, probably owing to the salt formation.

Compound	IS(J)	FS(N)	$T_{dec}(^{\circ}\mathrm{C})$
1	30	>360	144
2	28	>360	193
3	12	324	157
4	20	>360	350
5	15	>360	243
6	6	240	217
7	14	360	252

Table 2. Sensitivities and decomposition temperatures of the compounds

Additionally, non-isothermal kinetic calculations of compound **3** and **4** were done by using the temperature data of the first exothermic peaks of the DSC curves. The DSC curves were obtained based on four different heating rates (5,10,15 and 20 K·min⁻¹). Kissinger's method^[22] and Ozawa–Doyle's method^[23] were used, and equations of the two methods are shown as follows, respectively:

$$\ln \frac{\varphi}{T_m^2} = \ln \frac{AR}{E_a} - \frac{E_a}{RT_m}$$
(1)

$$\lg \varphi + \frac{0.4567E_a}{RT_m} = C \tag{2}$$

where φ is the heating rate, K·min⁻¹; R is the universal gas constant, 8.314 J·(mol·K)⁻¹; T_m is the temperature of the exothermic peak, K; Ea is the apparent activation energy, kJ·mol⁻¹; A is the pre-exponential factor, s⁻¹; and C is a constant.

Non-isothermal kinetic parameters of compound **3** and **4** are given in Table 3.

Apparent activation energy can be approximated to reflect the difficult degree of the thermal decomposition of the compound. The results using both methods correspond well with each other and the Arrhenius equation can be expressed as follow:

$$\ln k = 23.46 - \frac{99.8 \times 10^3}{RT}$$
(3) for compound **3**
$$\ln k = 48.86 - \frac{274.6 \times 10^3}{RT}$$
(4) for compound **4**

Which can be used to estimate the rate constants of the initial thermal decomposition process of the compound **3** and **4**. Compound **4** possesses high apparent activation energy, which reveals a very good thermal stability.

	Kissinger's method		<mark>Ozawa–Doyle's method</mark>	
Parameters	<mark>3</mark>	<mark>4</mark>	<mark>3</mark>	<mark>4</mark>
Apparent activation energy E_a (kJ·mol ⁻¹)	<mark>99.8</mark>	<mark>274.6</mark>	<mark>101.7</mark>	<mark>270.9</mark>
Pre-exponential factor <i>lg A</i>	<mark>10.19</mark>	<mark>21.22</mark>	<mark>-</mark>	-
The linear correlation coefficient	<mark>-0.9914</mark>	<mark>-0.9968</mark>	<mark>-0.9924</mark>	<mark>-0.9970</mark>
Standard deviation	<mark>0.09020</mark>	<mark>0.05685</mark>	<mark>0.03929</mark>	<mark>0.02471</mark>

 Table 3. Non-isothermal kinetic parameters of compound 3 and 4

It is noteworthy that compound **4** is featured with both superior thermal behavior (350 $^{\circ}$ C) and satisfying sensitivities (IS: 20 J, FS: >360 N), which highlights it as a potential stable explosive. It appears that the strong interactions born of intermolecular and intramolecular hydrogen bonding as well as the wavelike layered crystal packing together account for its high thermal stability and insensitivities. As a whole, the wavelike construction makes it easy to circulate the energy due to flexible up-and-down movements, in case of heat accumulation; as far as each individual layer concerned, the

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arch structure is always favored in architecture because it is characteristic of distributing the load to different parts so as to avoid localized stress concentration issue, herein it comes into play, resulting in the satisfying insensitivities of compound **4** to some extent. What an ingenious way of different things adapting themselves to this complicated world spontaneously. This kind of layer stacking mode with arch layers alternately arranged may provide some enlightening thinking to design new highly thermal stable and insensitive energetic materials.

The heat of formation $(\Delta_f H^{\circ}(s, M))$ of compound **3** was determined by using oxygenbomb calorimeter, and the molar standard enthalpies of formation (ΔH_m) was calculated to be -261.1 kJ·mol⁻¹, then the detonation parameters of compound **3** were calculated based on the values of density and the heat of formation using the EXPLO5 V5.05 computer code. The results are listed in Table 4.

	Compound 3
$V_{Det.}/$ m·s ^{-1 a}	7779
$T_{Det.}/{ m K}$ b	2117.98
<i>P_{CJ}</i> /GPa ^c	21.40
$H_{Det.}/\mathrm{kJ}\cdot\mathrm{Kg}^{-1}\mathrm{d}$	-2536.39
$V_g/\mathrm{dm^3\cdot Kg^{-1e}}$	844.06

 Table 4. Detonation parameters of compound 3 by EXPLO5 V5.05

^a Detonation velocity; ^b Detonation temperature; ^c Detonation pressure; ^d Heat of detonation; ^e Volume of gas at STP.

Compound **3** exhibits a moderate detonation velocity of 7800 $\text{m}\cdot\text{s}^{-1}$ approximately, keeping a reasonable balance between energy and safety in consideration of its relatively low sensitivities towards mechanical stimuli, which supports its application potential.

Conclusion

In summary, five salts of 3,6-bishydrazinium-1,2,4,5-tetrazine (BHT) were synthesized and fully characterized by elemental analysis, FT-IR and mass spectra, of which two

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crystal structures $(BHT_2-(NTO)_3$ (3) and $BHT-BTT\cdot 2H_2O$ (4)) were obtained and investigated. Besides acceptable sensitivities, all compounds display splendid thermal behavior simultaneously, with most of them being comparable to RDX if not better, maybe as a consequence of salt formation. The thermodynamics parameters of 3 and 4 were calculated via Kissinger's method and Ozawa–Doyle's method.

Compound **3** keeps a reasonable balance between energetic performance and safety, showing the application potential. Compound **4** is featured with both high thermal stability and insensitivities. The observed strong interactions and arch layer stacking are likely to contribute to its stability and insensitivities, providing a new thinking to design new highly stable energetic materials.

Experimental Section

Synthesis of BHT₂-(NTO)₃(3)

Sodium 3-nitro-1,2,4-triazolate-5-one (0.304g, 2mmol) was dissolved in water (5mL). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride (0.215g, 1mmol) in water (5mL). The mixture was stirred at ambient temperature and was then stored at 2 °C for 24h. Afterwards dark red crystals were filtered off.

EA: found(calc): C 17.65 (17.73), H 3.18 (3.10), N 57.79 (57.90); IR (KBr, cm⁻¹): v=3319, 2738, 1615, 1502, 1350, 1303, 1055, 779, 631, 605; Mass spec: 259.15[2C₂H₂N₄O₃].

Synthesis of BHT-BTT (4)

Sodium 4,5-Bis(tetrazol-5-yl)-1,2,3-triazolate (0.227g, 1mmol) was dissolved in water (10mL). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride (0.215g, 1mmol) in water (5mL). The mixture was stirred at ambient temperature and was then stored at 2 °C for 24h. Afterwards light orange crystals were filtered off.

EA: found(calc): C 18.87 (18.80), H 3.44 (3.39), N 69.37 (69.45); **IR** (**KBr**, cm⁻¹): v=3502, 3382, 3290, 3025, 1846, 1656, 1587, 1447, 1210, 1058, 995, 695, 586; **Mass**

spec: 347.7.

Synthesis of BHT-(DNP)₂ (5)

Sodium 3,4-dinitro-pyrazolate (0.36g, 2mmol) was dissolved in water (5mL). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride (0.215g, 1mmol) in water (5mL). A yellow powder precipitated suddenly. The powder was filtered off, washed with cold water and dried.

EA: found(calc): C 21.12 (20.96), H 2.27 (2.18), N 48.83 (48.91); **IR** (**KBr**, cm⁻¹): v=3301, 3216, 3008, 2931, 1643, 1535, 1453, 1056, 1001, 938, 744, 563; **Mass spec:** 157.10[C₃HN₄O₄⁻], 143.05[C₂H₇N₈⁺].

Synthesis of BHT-(NATr)₂ (6)

Sodium 3-nitroamino-1,2,4-triazolate (0.302g, 2mmol) was dissolved in water (5mL). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride (0.215g, 1mmol) in water (5mL). A brown powder precipitated suddenly. The powder was filtered off, washed with cold water and dried.

EA: found(calc): C 18.08 (18.00), H 3.11 (3.00), N 62.92 (63.00); IR (KBr, cm⁻¹): v=3414, 3269, 3161, 2926, 1598, 1535, 1467, 1390, 1327, 1241, 1051, 952, 771, 708; Mass spec: 128.15[C₂H₂N₅O₂⁻].

Synthesis of BHT-(FOX-7)₂ (7)

Sodium 1,1-diamino-2,2-dinitroethylene (0.34g, 2mmol) was dissolved in water (5mL). This solution was added to a stirred solution of 3,6-bishydrazinium-1,2,4,5-tetrazine dichloride (0.215g, 1mmol) in water (5mL). A yellow brown powder precipitated suddenly. The powder was filtered off, washed with cold water and dried.

EA: found(calc): C 16.51 (16.44), H 3.26 (3.20), N 51.08 (51.14); IR (KBr, cm⁻¹): v=3406, 3322, 3296, 1625, 1500, 1468, 1389, 1193, 1159, 1136, 1018, 753, 623; Mass spec: 146.70[C₂H₃N₄O₄⁻].

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