The Crystal Structure and Synthesis Mechanism of 3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (BDT): A Key Precursor of S-tetrazine

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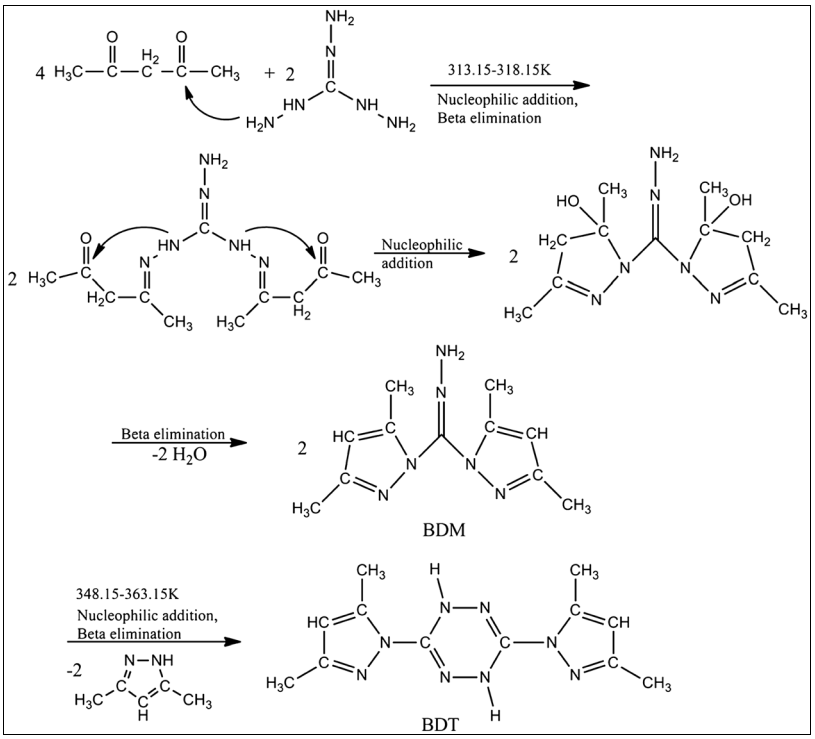

The single crystal structure of 1,1′-bis (3,5-dimethyl-pyrazole) methenehydrazine (BDM) was determined by X-ray single crystal diffraction for the first time. The obtained experimental results indicated that BDM was the intermediate of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (BDT), which was the key precursor of s-tetrazine. By this evidence, the preparation mechanism of BDT was proved: At 318.15 K, triaminoguanidine and pentanedione reacted to achieve the intermediate (BDM) by molecular nucleophilic addition and intramolecular nucleophilic substitution; when heated to 363.15 K, BDT was then generated by two molecules of BDM with nucleophilic substitution reaction. Furthermore, the thermal decomposition properties and also the non-isothermal kinetic parameters have been investigated in the present work.

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INTRODUCTION

High nitrogen heterocyclic compounds have developed into a series of promising energetic materials in recent years and attracted researchers all over the world into the five membered (imidazole, triazole, furazan) and six membered (tetrazine, triazine) heterocyclic compounds [1]. All these compounds have some common points: high enthalpy of formation, which mainly comes from the high energy N–N bonds, C–N bonds, and the large ring strain; relatively high melting point, just because of the high dense molecular structures and the large amount of hydrogen bonds in their nitrogen and hydrogen systems; the lone pair electrons of nitrogen atoms participated the conjugated system, increasing the aromaticity and thermal stability of the whole molecule; environmental harmony, just only giving out N_2 and CO_2 mostly when combust completely; moreover, some of these energetic materials show low sensitivity to static electricity, friction, and impact. All of these mentioned earlier make high nitrogen heterocyclic compounds as promising applications in the fields of propellants, low smoke and residues pyrotechnics, and new insensitive explosives [2–6].

Among these high nitrogen heterocyclic compounds, tetrazine was a typical six membered heterocyclic compound with high nitrogen content of 68.3%, just lower than 80.0% of the tetrazole. And tetrazine ring was

effective and outstanding in building structural unit in the High-energy Insensitive Energetic Materials design, especially the 1,2,4,5-tetrazine (s-tetrazine) ring [6–8]. Many researchers have done a lot of work on the s-tetrazines all over the world not just only for their good stability but also for the outstanding chemical properties they have shown[2,9,10]. Hiskey [1,5,8–13] reported the synthesis method and performances of a series of tetrazines, and Klapötke [14–16] also have done a lot of work on the tetrazine, both in theoretical and experimental aspects.

3,6-Bis (3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (BDT) was the most essential intermediates to synthesize the promising high nitrogen energetic compounds of s-tetrazine. At the same time, they can also serve as ligands to prepare some significant complexes. Therefore, in-depth analysis of their crystal structures and synthesis mechanism are particularly important. Although many researchers have done a lot of work on BDT, but the preparation mechanism of BDT has not been proven yet [13].

In order to take a deep study into the synthesis mechanism of BDT, meaningful experiments have been taken. The crystal structure of 1,1′-bis (3,5-dimethyl-pyrazole) methenehydrazine (BDM) as the intermediate of BDT has been determined by X-ray diffraction for the first time; as evidence, the synthesis mechanism of BDT has been proven at the same time. One step further, the thermal decomposition mechanism and non-isothermal kinetic parameters were also studied in present work.

EXPERIMENTAL

General caution. The titled compounds are energetic and tend to kindle or even explode under certain conditions. Appropriate safety precautions (safety glasses, face shields, leather coat, and ear plugs) should be taken, especially when these compounds are prepared on a large scale.

Material and physical technique. All chemical reagents and solvents of analytical grade were bought from the reagents company (Sinopharm Chemical Reagent Beijing Co., Ltd., Beijing, China) and used as supply. Triaminoguanidine hydrochloride was purchased commercially and recrystallized twice with distilled water before use.

Elemental analyses were performed on a Flash EA 1112 full-automatic trace element analyzer. DSC and TG–DTG measurements were carried out by using Pyris-1 differential scanning calorimeter and Pyris-1 thermogravimetric analyzer (Perkin Elmer, USA) under dry nitrogen atmosphere with a flowing rate of 20 mL min^{-1}. And the crystals were determined by using Rigaku Saturn 724^+ CCD detector diffractometer with graphite monochromatic Mo Kα radiation (λ = 0.07107 nm).

Synthesis. BDM: a solution with triaminoguanidine hydrochloride (9.00 g, 0.075 mol) dissolved with 60 mL deionized water was charged into three-necked flask. Then, pentanedione (15.00 mL, 0.15 mol) was slowly dropped at 318.15 K with strong stir for 1 h. The solution was cooled down to room temperature slowly. And precipitate was collected by filtration, washed with distilled water, and dried in explosion-proof water-bath dryer. Elemental analysis of BDM (C11N6H16) (%): calculated: C,56.90; N,36.21;H,6.90; found: C,56.93;N,36.22;H,6.85.

BDT: triaminoguanidine hydrochloride (9.00 g, 0.075 mol) was dissolved into deionized water(60 mL). The resulting solution was kept in 318.15 K, and dropwise addition was taken for Pentanedione (15 mL, 0.15 mol), stirring for 1 h. Then increasing to 363.15 K slowly, refluxing and stirring for an additional 1 h. Afterward, the solution was cooled down to room temperature slowly, filtering and washing with plenty distilled water. The residue was dried in explosion-proof water-bath dryer. Elemental analysis of BDT (C12N8H16) (%): calculated: C,52.92;N,41.23;H,5.85; found: C,52.94;N,41.18;H,5.88.

Data collection and structure determination. After few days' growing, a yellow flaky crystal of BDM and a colorless block single crystal for BDT were chosen for X-ray determination. The X-ray diffraction data collection was performed on a Rigaku AFC-10/Saturn 724^+ CCD detector diffractometer with graphite monochromatic Mo Kα radiation (λ = 0.071073 nm). The structures were solved by direct methods using SHELXS-97[17] and refined by full-matrix least squares methods on F^2 with SHELXL-97[18]. All non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least squares on F^2. Detailed information concerning crystallographic data collection and structures refinement are summarized in Table 1.

CCDC 884108 and 884109 contains 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.

RESULTS AND DISCUSSION

Structure description. The molecular structure views were shown in Figure 1, and the cell stacking views were shown in Figure 2, the selected bond distances and angles were listed in Table 2, 3, and the hydrogen bond lengths and angles were listed in Table 4.

In BDM molecule, there were two pyrazole rings and a half-tetrazine ring. These rings were non-coplanar. And the three ring plane equations were as follows: C(6)-N(3)-N(4) (flat A): $0.5691x - 0.8177y + 0.0865z = -0.4524$; C(8)-C(9)-C(10)-N(6)-N(5) (flat B): $0.3220x - 0.5530y\ 0.7684z = -15.1096$; C(2)-C(3)-C(4)-N(2)-N(1) (flat C): $-0.9841x + 0.1117y - 0.1381z = -0.6591$. Because of the steric effects, the two pyrazole rings have a rather big angle of 74.184°, which made the whole molecule low-energy and stable. And the angle of C(6)-N(3)-N(4) was 120.2°, similar with the interior angle of six-membered ring. These might enlarge the substitution reaction ability of the whole molecule. All these characteristics made BDM easy to eliminate a pyrazole ring when the molecule was attacked from N(4) by another one.

There were two types of hydrogen bonds in BDM molecule, intramolecular and intermolecular hydrogen bonds. Just as shown in the cell stacking view and the table list, the intramolecular hydrogen bonds, such as N(4)–H(4)A. . .N(5)

Table 1

Crystal data and structure refinement parameters.

	BDM	BDT
Empirical formula	$C_{11}H_{16}N_6$	$C_{12}H_{16}N_8$
Formula mass	232.30	272.33
Crystal system	*monoclinic*	*monoclinic*
Space group	$P2_1/n$	$P2_1$/c
Temperature (K)	153(2)	93(2)
Z	4	4
a, b, c (nm)	6.795(7), 6.893(7), 26.910(3)	12.776(4), 11.426(3), 9.095(3)
h, k, l	−8–8,−8–8,−34–34	−16–16,−14–10,−11–10
β (°)	90.860(11)	90.808(4)
V (Å^3)	1260(2)	1323.1(6)
D_c (g cm^{-3})	1.224	1.367
μ (Mo K$_\alpha$) (mm^{-1})	0.081	0.092
F(0 0 0)	496	576
θ Range (°)	3.03–27.51	3.19–27.50
Measured reflections	8989	10618
Unique data	2822 [R_{int} = 0.1357]	3020 [R_{int} = 0.0243]
R_1, wR_2 [I > 2σ(I)]	R_1 = 0.2089, wR_2 = 0.4827	R_1 = 0.0419, wR_2 = 0.1103
R_1, wR_2 (all data)	R_1 = 0.2495, wR_2 = 0.5037	R_1 = 0.0499, wR_2 = 0.1169
Goodness of fit	1.001	0.999
δp_{max}, δp_{min} (e nm^{-3})	0.904, −0.552	0.261, −0.260

BDM, 1,1′-bis (3,5-dimethyl-pyrazole) methenehydrazine; BDT, 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine.
[a] $w = 1/[\sigma 2(F_o^2) + (0.0748p)^2 + 0.1600p]$, $p = (F_o^2 + 2F_c^2)/3$.

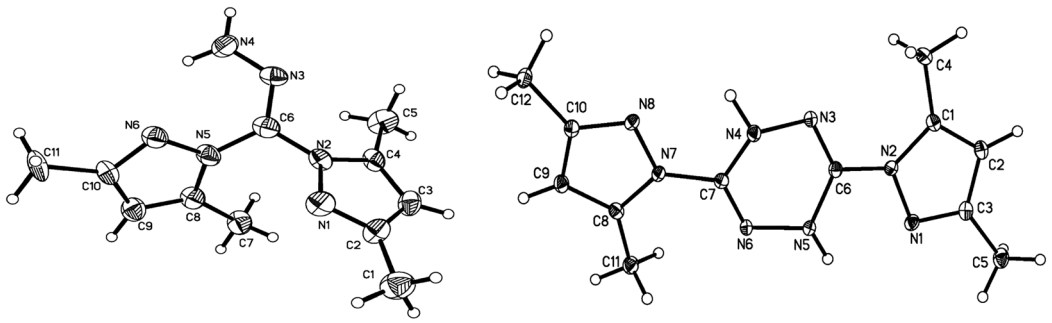


Figure 1. The molecular structures of the 1,1′-bis (3,5-dimethyl-pyrazole) methenehydrazine (BDM) and 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (BDT).

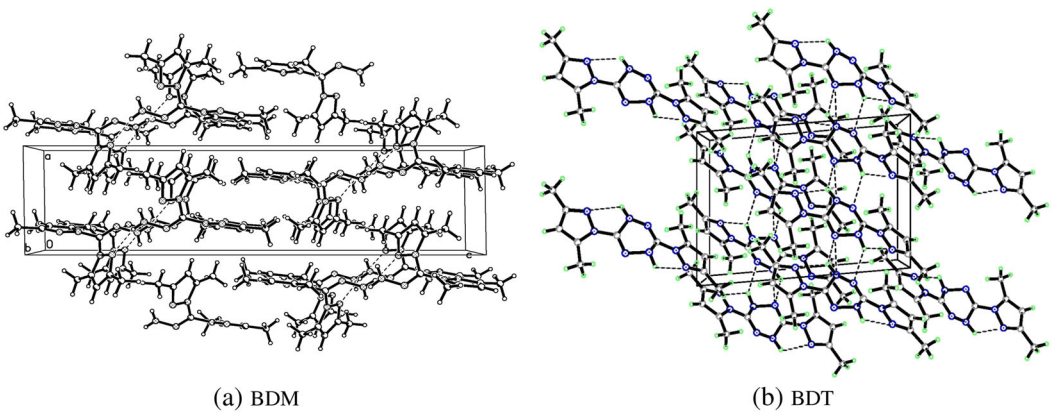


Figure 2. The views of stacking unit cell for 1,1′-bis (3,5-dimethyl-pyrazole) methenehydrazine (BDM) and 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (BDT).

Table 2

Selected bond lengths (Å) and bond angles (°) of BDM.

Bond	Dist.	Bond	Dist.	Bond	Dist.
N(1)–C(2)	1.326(11)	N(5)–C(8)	1.384(11)	C(3)–C(4)	1.361(13)
N(1)–N(2)	1.392(9)	N(5)–N(6)	1.390(9)	C(4)–C(5)	1.500(11)
N(2)–C(4)	1.387(9)	N(5)–C(6)	1.411(12)	C(7)–C(8)	1.516(11)
N(2)–C(6)	1.401(11)	N(6)–C(10)	1.365(11)	C(8)–C(9)	1.334(12)
N(3)–C(6)	1.294(11)	C(1)–C(2)	1.497(13)	C(9)–C(10)	1.384(13)
N(3)–N(4)	1.345(11)	C(2)–C(3)	1.439(13)	C(10)–C(11)	1.502(12)
Angle	(°)	Angle	(°)	Angle	(°)
C(2)-N(1)-N(2)	105.3(7)	N(1)-C(2)-C(3)	110.2(8)	N(2)-C(6)-N(5)	115.7(7)
C(4)-N(2)-N(1)	111.6(7)	N(1)-C(2)-C(1)	121.3(9)	C(9)-C(8)-N(5)	106.4(8)
C(4)-N(2)-C(6)	128.6(7)	C(3)-C(2)-C(1)	128.5(9)	C(9)-C(8)-C(7)	132.8(9)
N(1)-N(2)-C(6)	119.3(6)	C(4)-C(3)-C(2)	107.1(7)	N(5)-C(8)-C(7)	120.6(8)
C(6)-N(3)-N(4)	120.2(8)	C(3)-C(4)-N(2)	105.7(7)	C(8)-C(9)-C(10)	109.0(9)
C(8)-N(5)-N(6)	110.4(7)	C(3)-C(4)-C(5)	131.6(8)	N(6)-C(10)-C(9)	109.6(8)
C(8)-N(5)-C(6)	130.3(7)	N(2)-C(4)-C(5)	122.7(8)	N(6)-C(10)-C(11)	119.4(8)
N(6)-N(5)-C(6)	119.2(7)	N(3)-C(6)-N(2)	118.6(8)	C(9)-C(10)-C(11)	131.0(8)

BDM, 1,1′-bis (3,5-dimethyl-pyrazole) methenehydrazine.

Table 3

Selected bond lengths (Å) and bond angles (°) of BDT.

Bond	Dist.	Bond	Dist.	Bond	Dist.
N(1)–C(3)	1.325(2)	N(4)–C(7)	1.392(2)	N(7)–C(7)	1.399(2)
N(1)–N(2)	1.380(1)	N(5)–N(6)	1.433(1)	N(8)–C(10)	1.414(2)
N(2)–C(1)	1.379(2)	N(5)–C(6)	1.379(2)	C(1)–C(2)	1.364(2)
N(2)–C(6)	1.398(2)	N(6)–C(7)	1.274(2)	C(1)–C(4)	1.491(2)
N(3)–C(6)	1.277(2)	N(7)–N(8)	1.374(1)	C(2)–C(3)	1.414(2)
N(3)–N(4)	1.444(1)	N(7)–C(8)	1.379(2)		
Angle	(°)	Angle	(°)	Angle	(°)
C(6)-N(3)-N(4)	110.65(10)	N(8)-N(7)-C(8)	111.93(10)	N(1)-C(3)-C(2)	110.95(11)
C(7)-N(4)-N(3)	112.84(9)	N(8)-N(7)-C(7)	117.51(10)	N(1)-C(3)-C(5)	120.02(12)
C(6)-N(5)-N(6)	114.34(10)	C(8)-N(7)-C(7)	130.47(11)	C(2)-C(3)-C(5)	129.02(12)
C(7)-N(6)-N(5)	110.62(10)	C(1)-N(2)-C(6)	129.92(11)	C(9)-C(8)-N(7)	105.40(11)
N(3)-C(6)-N(5)	123.14(11)	N(1)-N(2)-C(6)	116.86(10)	C(9)-C(8)-C(11)	129.87(11)
N(3)-C(6)-N(2)	121.15(11)	C(10)-N(8)-N(7)	105.01(10)	N(7)-C(8)-C(11)	124.73(11)
N(5)-C(6)-N(2)	115.68(11)	C(2)-C(1)-N(2)	105.28(11)	C(8)-C(9)-C(10)	106.72(11)
N(6)-C(7)-N(4)	123.32(11)	C(2)-C(1)-C(4)	130.12(11)	N(8)-C(10)-C(9)	110.93(11)
N(6)-C(7)-N(7)	120.79(11)	N(2)-C(1)-C(4)	124.56(11)	N(8)-C(10)-C(12)	120.23(11)

BDT, 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine.

Table 4

Hydrogen bond lengths (Å) and bond angles (°).

d(D–H···A)	d(D–H)	d(H···A)	d(D···A)	∠DHA
BDM-N(4)-H(4)A. . .N(5)	0.88	2.48	2.794	101
BDM-N(4)-H(4)A. . .N(6)	0.88	2.42	2.956	119
BDM-N(4)-H(4)B. . .N(6)#1	0.88	2.18	3.039	164
BDT-N(5)-H(1). . .N(1)	0.94	2.19	2.620	106
BDT-N(5)-H(1). . .N(3) #1	0.94	2.17	2.917	135
BDT-N(4)-H(4). . .N(8)	0.93	2.19	2.641	108
BDT-N(4)-H(4). . .N(6) #2	0.93	2.28	3.027	137
BDT-C(4)-H(4)B. . .N(3)	0.98	2.60	2.935	100

BDM, 1,1′-bis (3,5-dimethyl-pyrazole) methenehydrazine; BDT, 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine.
Symmetry transformations for BDM: #1:1/2 − x, −1/2 + y, 1/2 − z.
Symmetry transformations for BDT: #1: x, 1/2 − y, 1/2 + z; #2: x, 1/2 − y, −1/2 + z.

and N(4)–H(4)A. . .N(6), linked with the neighboring bonds to form a large amount of stable five-membered or six-membered rings. All these rings formed a 2-D lamellar structure, and the intermolecular hydrogen bonds, just like N(4)–H(4)B. . .N(6), connected the 2-D structure into a regular 3D network that was much more stable in a larger scale.

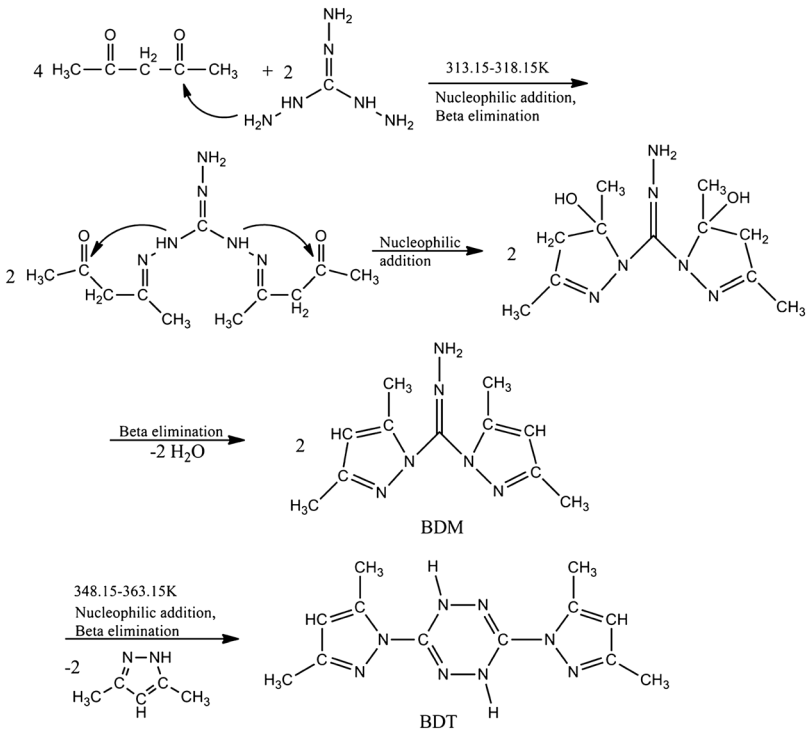
In BDT molecule, two hydrogen atoms were separated on different sides of the tetrazine ring, which made the whole molecule more balance and stable. And there were also two flats in the BDT molecule: N(2)-N(3)-N(5)-C(6) (flat D): $0.6481x + 0.4849y - 0.5837z = 6.5801$; N(4)-N(6)-N(7)-C(7) (flat E): $0.2664x + 0.8761y - 0.4019z = 7.9657$. The two flats had an included angle of 33.55°. The pyrazole rings in the molecule were slightly distorted, the dihedral angles of C(3)-N(1)-N(2)-C(1) and N(2)-N(1)-C(3)-C(2) were 0.58° and −0.20°, homogeneously, N(2)-C(1)-C(2)-C(3) and C(1)-C(2)-C(3)-N(1) have dihedral angles of 0.57°and −0.24°. Meanwhile, the interior angles of pyrazole rings also twisted lightly, 1.28–3.93°, comparing with standard planar five-membered ring. The distortion of the whole molecule also had an influence upon the bond length. The bond length of N(3)-N(4) was 1.433 Å, that of N(5)-N(6) was 1.444 Å, and they were both close to the N–N bond. In the meantime, the length of N(1)-N(2) was 1.380 Å and the length of N(7)-N(8) was 1.374 Å, also close to the N═N bond.

Many intramolecular and intermolecular hydrogen bonds of BDT built up a huge 3D network. All these hydrogen bonds may divide into three categories. One was the intramolecular hydrogen bonds between N–H of tetrazine rings and N atoms of the homolateral pyrazole rings, such as N(5)–H(1). . .N(1) bond with a length of 2.620 Å. These hydrogen bonds formed steady five-membered rings with the neighboring bonds. Two was the faintish weaker intramolecular hydrogen bonds between the Me-H of the pyrazole rings with N atoms of tetrazine rings on the same side, such as C(4)–H(4)B. . .N(3) hydrogen bond with the length of 2.935 Å. These hydrogen bonds formed six-membered rings with the neighboring bonds. Three was the intermolecular hydrogen bonds that connected the molecule into a huge network in a larger scale.

Synthesis mechanism of BDT. The crystal structure of BDM as the evidence had indicated that the synthesis of BDT can be divided into two section: firstly, the formation of BDM under 318.15 K; secondly, the generation of BDT under 348.15–363.15 K and refluxing condition. Scheme 1 has shown the mechanism of BDT preparation.

At 318.15 K, intermolecular nucleophilic addition reaction initiated by the aggression of the two hydrazine terminal amino groups of triaminoguanidine to the carbonyl carbon atom during which eliminated two molecules of H_2O; then the amino attacked the carbonyl carbon atom, leading to the occurrence of intramolecular nucleophilic substitution reaction that also eliminated two molecules of H_2O; in the meantime, BDM was generated; when heated to 363.15 K, the intermolecular nucleophilic substitution between two molecules of BDM bechanced, eliminating two molecules of pyrazole and generating one molecule of BDT. Just as

Scheme 1. The synthesis mechanism of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (BDT).



shown in Scheme 1, the probability of nucleophilic addition reaction between carbonyl carbon and the two distinct amino groups is completely different.

Thermal decomposition. For the purpose of investigating the thermal behavior of the two compounds of BDM and BDT, the DSC and TG–DTG tests have been conducted under the linear heating rate of 10 K min^{-1} in N_2 atmosphere at the flowing rate of 20 mL min^{-1}, and the curves are shown in Figures 3 and 4, respectively.

It could be seen from the curves that BDM decomposed directly, without melting, and the exothermic decomposition process was in 373.15–399.35 K range with a peak temperature of 384.05 K. It also could be observed from the TG–DTG curve that the major weight loss of 92.67% occurred at 383.55–499.45 K range, and the maximum weight loss rate corresponded to 473.35 K, and from 499.45 to 773.15 K, kept on losing weight slowly until no remaining residue.

As for BDT, the thermal decomposition included an endothermic process and an exothermic process between 323.15 and 773.15 K. At 407.35–435.45 K, BDT melt first with a melting peak temperature of 422.65 K, and then decomposed at 509.65–587.75 K temperature range with an exothermic enthalpy of 681.2 J g^{-1}. There was an exothermic temperature peak of 539.05 K in the process. At 418.35–525.95 K temperature range, BDT performed a rapid weight loss, maximum weight loss rate occurred at 522.35 K, and the total weight loss of this process was 87.8%; between 522.25 and 773.15 K, BDT showed a slow weight loss process with the weight loss of 12.2%, no remaining residue at last.

Non-isothermal kinetics analysis. Kissinger's method [19], Ozawa's method [20], and Starink's method [21] were widely used to study the kinetics parameters. The equations were just as follows:

$$\ln\beta/T_p^2 = \ln[RA/E_a] - E_a/RT_p \quad (1)$$

$$\log\beta + \frac{0.4567E_a}{RT_p} = C_1 \quad (2)$$

$$\ln \beta/T_p^{1.8} = C_2 - 1.0037E_a/RT_p, \quad (3)$$

where T_p was the peak temperature, K; R was the gas constant, 8.314 J K^{-1} mol^{-1}; β was the linear heating rate, K min^{-1}; C_1, C_2 were constant.

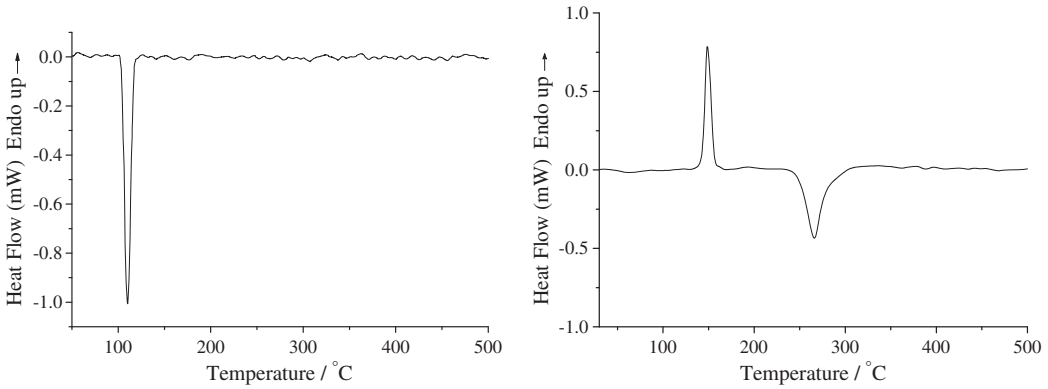


Figure 3. The DSC and TG–DTG curves of 1,1′-bis (3,5-dimethyl-pyrazole) methenehydrazine (BDM) under N_2 atmosphere with a heating rate of 10 K min^{-1}

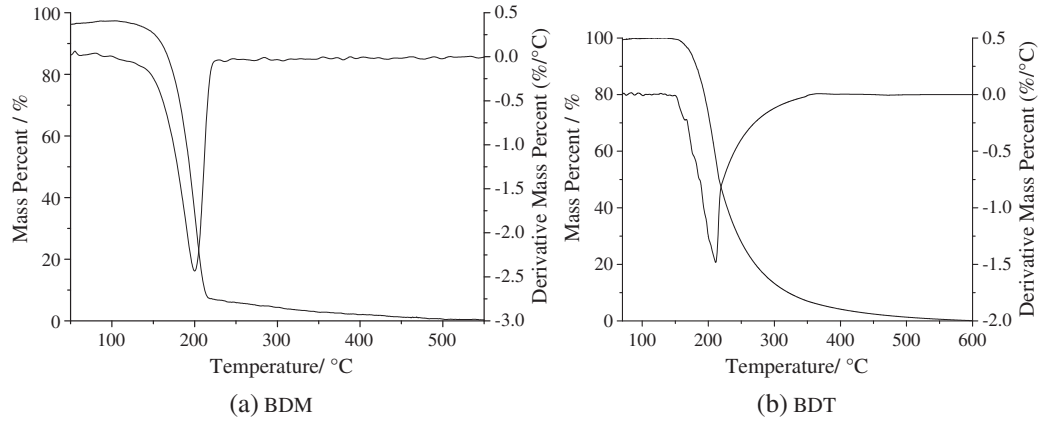


Figure 4. The DSC and TG–DTG curves of 3,6-bis(3,5-dimethylpyrazol-1-yl)-1,4-dihydro-1,2,4,5-tetrazine (BDT) under N_2 atmosphere with a heating rate of 10 K min^{-1}

Table 5

The peak temperatures of the first main exothermic at different heating rates and the chemical kinetics parameters.

Method	E (kJ mol^{-1})	R^2	Ln(A/s^{-1})
Kissinger's method[a]	86.67	0.9987	4.547
Ozawa–Doyle's method	90.94	0.9990	
Starink's method	87.24	0.9988	

[a] β (K min^{-1})/T_P (K): 5/522.56; 10/538.58; 15/549.51; 20/557.72.

With the peak temperatures measured under 5, 10, 15, and 20 K min^{-1} heating rates, the activation energy E, pre-exponential factor A, and linear correlation coefficient R were determined by the three methods just as shown in Table 5.

Take the average of the three calculated activation energy as the final one, 88.28 kJ mol^{-1}. In this way, the Arrhenius equations of BDT could be expressed as: $\ln k = 4.547 - 88.28 \times 10^3/(RT)$.

CONCLUSIONS

The single crystal structure of BDM as the intermediate of BDT has been determined by X-ray diffraction for the first time. And the synthesis mechanism of BDT has been proved in this paper. At 318.15 K, triaminoguanidine reacted with pentanedione to achieve the intermediate (BDM) by molecular nucleophilic addition and intramolecular nucleophilic substitution; when heated to 363.15 K, BDT was generated by two molecules of intermediate with nucleophilic substitution reaction.

For the purpose of investigating the thermal behavior of the two compounds, the DSC and TG–DTG have been conducted. BDM decomposed directly without melting; thermal decomposition of BDT included an endothermic process and an exothermic process. Non-isothermal kinetics analysis of BDT has been conducted by three different methods: Kissinger's method, Ozawa's method, and Starink's method. The results indicated that the Arrhenius Equation of BDT could be expressed as follows: $\ln k = 4.547 - 88.28 \times 10^3/(RT)$.

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