

Structural and Thermal Characteristics of a High-Nitrogen Energetic Material: G(AHDNE)

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A high-nitrogen energetic salt, 1-amino-1-hydrazino-2,2-dinitroethylene guanidine salt [G(AHDNE)], was synthesized by reacting of 1-amino-1-hydrazino-2,2-dinitroethylene (AHDNE) and guanidine hydrochloride in sodium hydroxide aqueous solution. The theoretical investigation on G(AHDNE) was carried out by B3LYP/6-311+G* method. The thermal behaviors of G(AHDNE) were studied with DSC and TG-DTG methods, and the result presents an intense exothermic decomposition process. The enthalpy, apparent activation energy and pre-exponential constant of the process are -1060 J g^{-1} , $148.7 \text{ kJ mol}^{-1}$ and $10^{15.90} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion of G(AHDNE) is $152.63 \text{ }^\circ\text{C}$. The specific heat capacity of G(AHDNE) was studied with micro-DSC method and theoretical calculation method, and the molar heat capacity is $314.69 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K . Adiabatic time-to-explosion of G(AHDNE) was calculated to be a certain value between 60-72 s. The detonation velocity and detonation pressure were also estimated. G(AHDNE) presents good performances.

Key Words : 1,1-Diamino-2,2-dinitroethylene (FOX-7), 1-Amino-1-hydrazino-2,2-dinitroethylene (AHDNE), Guanidine salt, Synthesis, Thermal properties

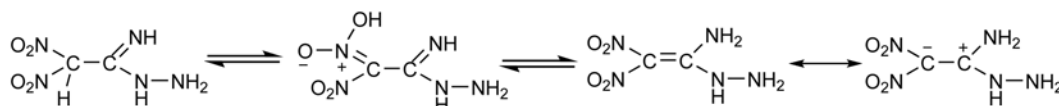
Introduction

“Push-pull” nitro-enamine is a kind of compound with special construction, which possesses a highly polarized carbon-carbon double bond with positive and negative charges being stabilized by the amino group and nitro group respectively, and exists in manifold tautomers and resonances.¹⁻³ 1,1-Diamino-2,2-dinitroethylene (FOX-7) is a novel high-energy material with high thermal stability and low sensitivity to impact and friction.⁴⁻¹¹ FOX-7 is also a representative “push-pull” nitro-enamine compound, presents certain acidic properties and can react with some nucleophiles to synthesize new high energy derivatives.^{2,3,5,12-15} Our interest mainly consisted in modifying molecular structure of FOX-7 in order to obtain some new high-energy compounds and research their structure-property relationship.¹⁶⁻²²

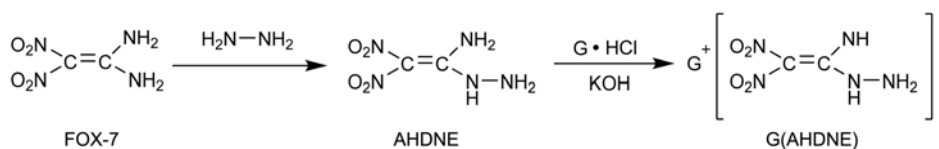
1-Amino-1-hydrazino-2,2-dinitroethylene (AHDNE) is a

derivative of FOX-7, has the same characteristics to FOX-7 and exists in many manifold tautomers and resonances (Scheme 1).^{17,18} AHDNE can also react with strong alkalis to prepare some new high-nitrogen energetic salts.²³ Gao *et al.* have also reported their results on the field.²⁴ 1-Amino-1-hydrazino-2,2-dinitroethylene guanidine salt [G(AHDNE)] was also prepared by our group through the designed route. The thermal stability of G(AHDNE) is good, nitrogen content can reach 50.4% and oxygen-balance value is -50.5% . Through synthesis of G(AHDNE), it is expected to increase energy and nitrogen content, produce more clean gas in thermal decomposition and combustion process, and use it as potential gas generator and additive in propellant.

In the paper, the structure characterization and thermal behaviors of G(AHDNE) were studied, specific heat capacity was determined, and adiabatic time-to-explosion and detonation properties were also calculated for estimating its



Scheme 1. Tautomers and resonances of AHDNE.



Scheme 2. Synthesis of G(AHDNE).

performances.

Experimental Section

Sample. AHDNE was prepared according to Refs. 17-18.

G(AHDNE) was prepared as follows: AHDNE (0.015 mol, 2.45 g) was suspended in 10 mL of water, two solutions of NaOH (0.02 mol, 1.2 g in 5 mL of water) and guanidine hydrochloride (0.025 mol, 2.39 g in 5 mL of water) were added drop wise to it, respectively. After reaction at room temperature for 30 min, the resulting mixture was slowly cooled to 0 °C. Many brown sediment of G(AHDNE) were formed, and then filtered, washed with methanol and dried under vacuum, yielding 1.87 g (56%) product with purity > 99%. Anal. Calcd.(%) for C₃H₁₀N₈O₄: C 16.22, H 4.54, N 50.44; found: C 16.13, H 4.67, N 50.16. IR (KBr): 3438, 3353, 1658, 1488, 1393, 1360, 1251, 1136, 1039, 905, 750 cm⁻¹.

Experimental Equipments and Conditions. The DSC experiments were performed using a DSC-Q200 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 50 mL min⁻¹. The heating rates used were 2.5, 5.0, 10.0 and 15.0 °C min⁻¹ from ambient temperature to 350.0 °C.

The TG-DTG experiment was performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL min⁻¹. The heating rate used was 10.0 °C min⁻¹ from ambient temperature to 550.0 °C.

The specific heat capacity (C_p) was determined using a Micro-DSCIII apparatus (SETARAM, France), the amount of used sample was 359.89 mg. The heating rate used was 0.15 °C min⁻¹ (2.5×10^{-3} K s⁻¹) from 10.0 to 80.0 °C.

Theoretical Calculation Investigation. A molecular unit of G(AHDNE) generated from Chem3D software was optimized by the minimum energy of MOPAC method repeatedly to non-change, and then selected as the initial structure model, while B3LYP/6-311+G* method in *Gaussian 03* package²⁵ was used to further optimize the structure and compute its frequencies at different temperatures. Meanwhile, the optimized parameters were used to further compute molecular volume for 100 times, and the average value was regarded as the credible molecular volume. All convergent precisions were the system default values, and all calculations were carried out on a *Lenovo* T260 server.

Results and Discussion

Theoretical Calculation Results. Vibration analysis showed that the optimized structure is in accord with the minimum points on the potential energy planes, which means no virtual frequencies, proving that the optimized structure is stable and calculation results are reliable. Optimized molecular geometry and parameters were shown in Figure 1 and Table 1.

From Figure 1, it can be seen that almost no change occurred on the steric configuration of AHDNE from molecule state to ion condition. Nitro-nitro plane is still perpendicular to the amino-hydrazino plane. Guanidine cation is in the side

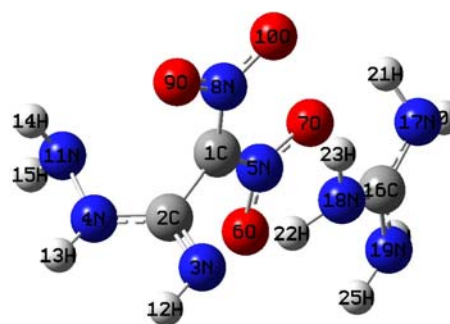


Figure 1. Optimized molecular structure of G(AHDNE).

of nitro groups of AHDNE anion. Guanidine cation plane is nearly parallel to the nitro-nitro plane of AHDNE anion. From Table 1, it can be seen that no obvious change occurred on the non-hydrogen bond lengths. Theoretical C-C double bond was further extended from 1.47 to 1.49 Å and more close to the C-C single bond (1.53 Å). The bond lengths of C(2)-N(3) and C(2)-N(4) are almost equal in AHDNE molecule, but are changed greatly in ion condition. C(2)-N(3) (1.29 Å) is still a typical conjugated C-N double bond (1.28 Å), but C(2)-N(4) is more close to C-N single bond (1.44 Å). In all, the obvious conjugative effect occurs between C(1)-C(2), C(2)-N(3) and C(2)-N(4). From the bond lengths of C(16)-N(17), C(16)-N(18) and C(16)-N(19), the N-C double bond in guanidine cation is conjugated and averaged. The dihedral angle of N(5)-C(3)-N(6)-N(7) is 176.4°, and the above four atoms are almost in one plane. So the structure formula of guanidine cation can be expressed as [C(NH₂)₃]⁺. But from the bond angles of N(17)-C(16)-N(18), N(17)-C(16)-N(19) and N(18)-C(16)-N(19), N(17)-C(16) still has some double bond vestige. From Milliken net charges of atoms, C(1) atom presents certain positive charges (0.1460 *e*), but C(2) atom has some negative charges (-0.0089 *e*), which is the typical characteristic of ‘push-pull’ nitro-enamine. The total atomic net charges of guanidine cation and AHDNE anion are close to 1 (-1), indicating that G(AHDNE) is made up of entire ions and is a typical ionic organic compound. All are in good agreement with that of 1,1-diamino-2,2-dinitroethylene guanidine salt [G(FOX-7)], which is a similar compound with G(AHDNE).¹⁹

Based on the simple harmonic oscillator analysis, 69 groups of frequency and intensity were obtained, only those large than 500 cm⁻¹ were listed in Table 2. The scaled IR frequencies were calibrated by multiplying 0.9614. Due to the complexity of vibrational mode, some typical vibrational modes were analyzed and compared with the experimental data. The theoretical value at 2946-3525 cm⁻¹ caused by the N-H stretching vibration is in agreement with that of the experiment (3353 and 3438 cm⁻¹). The asymmetric and the symmetric characteristic absorption peak characteristic of -NO₂ were found to be 1136 and 1353 cm⁻¹, relevant to the experimental value of 1136 and 1360 cm⁻¹. The theoretical values at 1258 cm⁻¹ caused by the C-NO₂ stretching vibration is consistent with that of the experiment (1251 cm⁻¹). The absorption peak of the C-C stretching vibration is found to

Table 1. Calculated non-hydrogen bond lengths, bond angles and Mulliken net charges of G(AHDNE) and comparison with AHDNE

Bond length/Å					
	G(AHDNE)	AHDNE		G(AHDNE)	AHDNE
C(1)-C(2)	1.49	1.47	N(5)-O(7)	1.25	1.24
C(1)-N(5)	1.38	1.38	N(8)-O(9)	1.25	1.24
C(1)-N(8)	1.39	1.38	N(8)-O(10)	1.25	1.24
C(2)-N(3)	1.29	1.29	C(16)-N(17)	1.35	
C(2)-N(4)	1.36	1.30	C(16)-N(18)	1.33	
N(4)-N(11)	1.39	1.39	C(16)-N(19)	1.34	
N(5)-O(6)	1.26	1.24			
Bond angles/(°)					
	G(AHDNE)	AHDNE		G(AHDNE)	AHDNE
C(2)-C(1)-N(5)	117.9	118.1	C(1)-N(5)-O(7)	122.6	122.5
C(2)-C(1)-N(8)	116.4	118.1	O(6)-N(5)-O(7)	121.8	121.3
N(5)-C(1)-N(8)	125.1	123.7	C(1)-N(8)-O(9)	115.2	116.3
C(1)-C(2)-N(3)	117.7	120.6	C(1)-N(8)-O(10)	123.0	122.5
C(1)-C(2)-N(4)	117.0	117.3	O(9)-N(8)-O(10)	121.8	121.3
N(3)-C(2)-N(4)	125.3	122.1	N(17)-C(16)-N(18)	120.7	
C(2)-N(4)-N(11)	120.1	120.1	N(17)-C(16)-N(19)	120.1	
C(1)-N(5)-O(6)	115.6	116.3	N(18)-C(16)-N(19)	119.1	
Mulliken net charges/e					
C(1)	0.1460		C(16)	0.1592	
C(2)	-0.0089		N(17)	-0.5877	
N(3)	-0.6433		N(18)	-0.7198	
N(4)	-0.3139		N(19)	-0.6281	
N(5)	-0.1985		H(20)	0.3776	
O(6)	-0.1169		H(21)	0.4137	
O(7)	-0.0041		H(22)	0.5034	
N(8)	-0.2057		H(23)	0.3938	
O(9)	-0.1358		H(24)	0.3783	
O(10)	-0.0400		H(25)	0.4174	
N(11)	-0.5205				
H(12)	0.3110				
H(13)	0.3539				
H(14)	0.3362				
H(15)	0.3327				
AHDNE ⁻	-0.7078		G ⁺	0.7078	

be at 1449 cm⁻¹, relevant to the experimental value of 1488 cm⁻¹.

Thermal Behaviors. The typical DSC curve (Figure 2) indicates that the thermal behaviors of G(AHDNE) present only one obvious exothermic decomposition process, and the extrapolated onset temperature, peak temperature and decomposition enthalpy are 162.90 °C, 166.15 °C and -1060 J g⁻¹ at the heating rate of 10.0 °C min⁻¹, respectively. Corresponding TG-DTG process occurs at 152-200 °C with a mass loss of about 49.5% (Figure 3). The thermal behaviors of G(AHDNE) are quite different from that of AHDNE whose thermal behavior presents two continuous decomposition processes, and the peak temperatures are 112.95 °C and 133.73 °C at the heating rate of 5.0 °C min⁻¹,¹⁸ respectively. G(AHDNE) has higher thermal stability than AHDNE. The thermal behaviors of G(AHDNE) are also quite different

from that of G(FOX-7).²⁶ Thermal behavior of G(FOX-7) can be divided into three obvious stages, the first stage is a melting process, the other two stages are the exothermic decomposition processes.

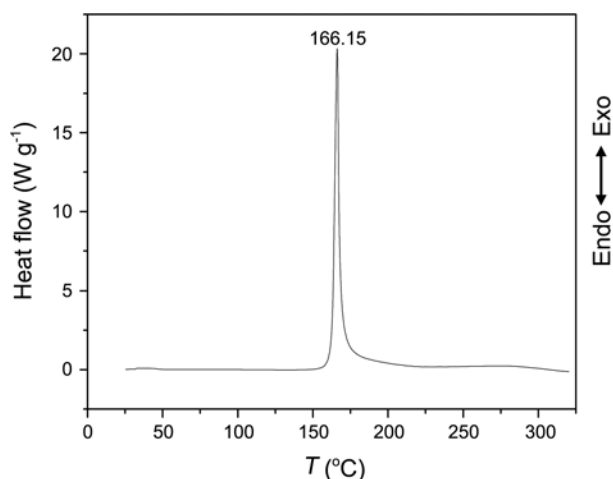
In order to obtain the kinetic parameters (the apparent activation energy (*E*) and pre-exponential constant (*A*)) of the exothermic decomposition reaction for G(AHDNE), a multiple heating method (Kissinger method²⁷ and Ozawa method²⁸) was employed (Figure 4). The Kissinger and Ozawa equations are as follows:

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

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

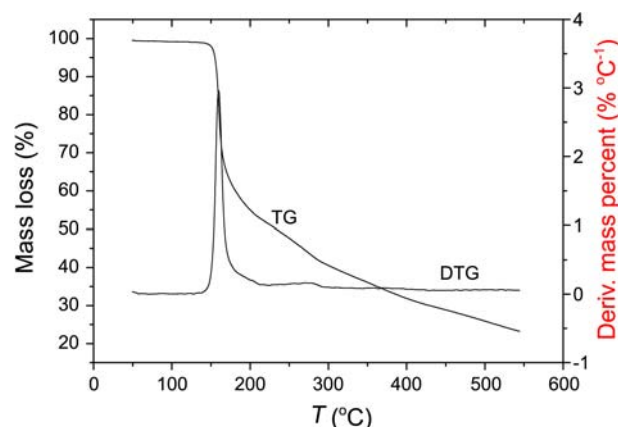
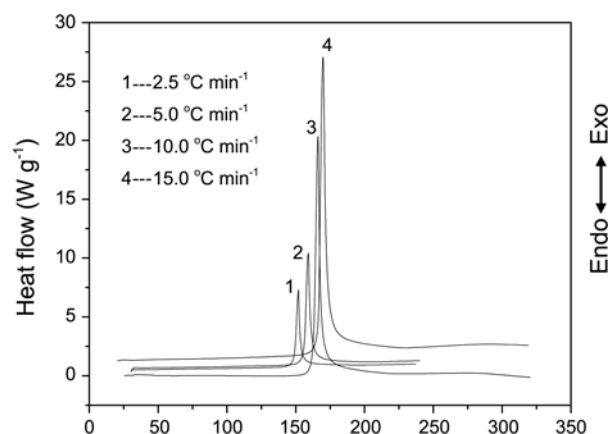
Table 2. Scaled IR frequencies for G(AHDNE)

ν /cm ⁻¹	I /(km mol ⁻¹)	Exptl /cm ⁻¹	ν /cm ⁻¹	I /(km mol ⁻¹)	Exptl /cm ⁻¹
502	33.87		1258	755.5	1251
523	54.4		1287	19.4	
568	31.8		1353	60.4	1360
603	104.9		1402	165.2	
609	22.6		1420	35.3	
615	312.1		1449	362.8	1488
634	53.8		1532	51.6	
655	128.2		1551	186.9	
727	9.5		1587	227.9	
738	161.5		1653	161.5	
747	157.6		1660	200.5	1658
756	38.0		1663	83.7	
767	68.0		1677	44.9	
808	128.5		2946	884.8	
856	353.3		3322	13.9	
968	2.0	905	3343	131.1	3335
1041	88.6		3394	23.2	
1106	12.3		3419	80.5	3438
1136	216.2	1136	3457	7.9	
1146	7.4		3485	46.4	
1152	3.8		3490	56.9	
1170	12.6		3514	57.9	
1200	28.6				

**Figure 2.** DSC curve of G(AHDNE) at a heating rate of 10.0 °C min⁻¹.

where T_p is the peak temperature (K), β is the linear heating rate (K min⁻¹), E is the apparent activation energy (kJ mol⁻¹), A is the pre-exponential constant (s⁻¹), R is the gas constant (J mol⁻¹ K⁻¹) and C is a constant.

The DSC measured values of the beginning temperature (T_0), extrapolated onset temperature (T_e), peak temperature (T_p) and enthalpy (ΔH_d) of the exothermic decomposition reaction were listed in Table 1. The values of T_{00} , T_{e0} and T_{p0} in the stage corresponding to $\beta \rightarrow 0$ obtained by Eq. (3) were also listed in Table 3.²⁹

**Figure 3.** TG-DTG curves of G(AHDNE) at a heating rate of 10.0 °C min⁻¹.**Figure 4.** DSC curves of G(AHDNE) at various heating rates.

$$T_{(0, e \text{ or } p)i} = T_{(00, e0 \text{ or } p0)} + n\beta_i + m\beta_i^2 \quad i = 1-4 \quad (3)$$

where n and m are coefficients.

The above-mentioned values (E and A) determined by Kissinger method and Ozawa method and linear correlation coefficients (r) were listed in Table 4. It can be seen that the apparent activation energy obtained by Kissinger method agrees well with that obtained by Ozawa method, and the linear correlation coefficients are all very close to 1. So, the result is credible. Moreover, the apparent activation energy of the exothermic decomposition reaction was lower, which indicates that G(AHDNE) is easy to decompose above 140 °C heating.

T versus α (the conversion degree) curves at different heating rates were shown in Figure 5. By substituting corresponding data from DSC experiments into Eq. (2), the values of E for any given value of α were obtained and shown in Figure 6. The values of E to the equal α steadily distribute from 133 to 143 kJ mol⁻¹ in the α range of 0.05-0.9, and the average value of E is 139.7 kJ mol⁻¹. It is in agreement with that obtained by Kissinger method and Ozawa method from only peak temperatures, which also indicates that the result is credible.

Critical Explosion Temperature. The critical temperature of thermal explosion (T_b) is an important parameter required

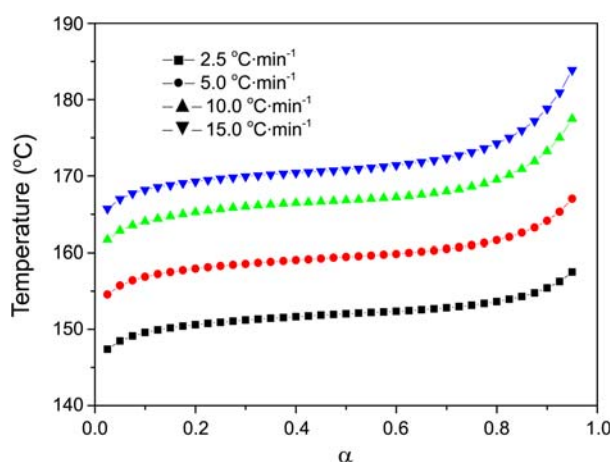
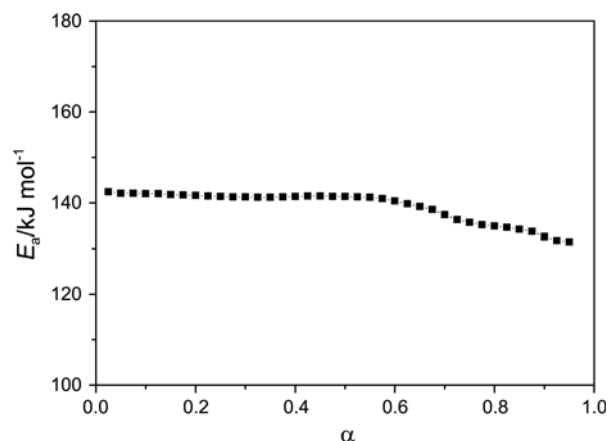
Table 3. The values of T_0 , T_e , T_p , ΔH_d , T_{00} , T_{e0} and T_{p0} of G(AHDNE) at various heating rates

$\beta/(\text{°C min}^{-1})$	$T_0/\text{°C}$	$T_e/\text{°C}$	$T_p/\text{°C}$	$\Delta H_d/(\text{J g}^{-1})$	$T_{00}/\text{°C}$	$T_{e0}/\text{°C}$	$T_{p0}/\text{°C}$
2.5	138.85	149.19	151.96	-1060.0	132.17	142.47	145.00
5.0	146.59	156.13	159.14				
10.0	152.16	162.90	166.15				
15.0	155.11	166.48	169.84				

Table 4. The kinetic parameters obtained by the data in Table 3

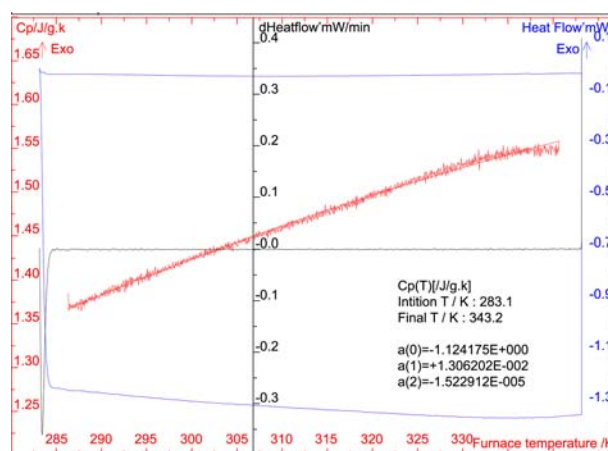
$E_k/(\text{kJ mol}^{-1})$	$\lg A$	r_k	$E_o/(\text{kJ mol}^{-1})$	r_o	$\bar{E}/(\text{kJ mol}^{-1})$
148.9	15.90	0.9994	148.4	0.9994	148.7

Subscript k, data obtained by Kissinger's method; subscript o, data obtained by Ozawa's method. \bar{E} is the mean value of apparent activation energy

**Figure 5.** T vs α curves for the decomposition reaction of G(AHDNE) at different heating rates.**Figure 6.** E_a vs α curve for the decomposition reaction of G(AHDNE) by Ozawa's method.

to insure safe storage and process operations for the energetic materials and then to evaluate the thermal stability, and can be obtained by Eq. (4).²⁹ The calculated T_b of G(AHDNE) was 152.63 °C, which is much higher than that of AHDNE as 98.16 °C.¹⁸ After AHDNE became guanidine salt, the thermal stability become better.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{e0}}}{2R} \quad (4)$$

**Figure 7.** Determination results of the continuous specific heat capacity of G(AHDNE).

where E_o is the apparent activation energy obtained by Ozawa method.

Specific Heat Capacity. Figure 7 shows the determination result of G(AHDNE), using a continuous specific heat capacity mode of Micro-DSCIII. In determined temperature range, specific heat capacity presents a good quadratic relationship with temperature. Specific heat capacity equation of G(AHDNE) is:

$$C_p(\text{J g}^{-1} \text{K}^{-1}) = -1.1242 + 1.3062 \times 10^{-2}T - 1.5229 \times 10^{-5}T^2 \quad (283.0 \text{ K} < T < 353.0 \text{ K}) \quad (5)$$

The molar heat capacity of G(AHDNE) is 314.69 J mol⁻¹ K⁻¹ at 298.15 K.

Table 6 shows the results of specific heat capacity by the theoretical calculation and experimental determination and their relative deviations (RD) at different temperatures. The calculated results are all less than the experimental results, and the relative deviations are greater, from 13.91% to 15.93%. The reason is only gas phase molecule was used in theoretical calculation process, which is clearly different from the actual solid phase.

Adiabatic Time-To-Explosion. The adiabatic time-to-explosion is also an important parameter for evaluating the thermal stability of energetic materials and can be calculated by Eqs. (6)-(7).^{18,26,29-33}

Table 5. Results of specific heat capacity obtained by theoretical calculation and experimental determination and their relative deviations at 283.0-353.0 K

Temperature /K	C_p /(J mol ⁻¹ K ⁻¹)		RD /%
	Theoretical calculation value	Experimental value	
283.0	243.91	300.51	18.83
288.0	246.89	305.36	19.15
293.0	249.84	310.04	19.42
298.0	252.76	314.55	19.64
303.0	255.66	318.89	19.83
308.0	258.54	323.07	19.97
313.0	261.40	327.07	20.08
318.0	264.23	330.91	20.15
323.0	267.04	334.57	20.18
328.0	269.82	338.07	20.19
333.0	272.58	341.40	20.16
338.0	275.32	344.56	20.09
343.0	278.03	347.54	20.00
348.0	280.71	350.36	19.88
353.0	283.38	353.02	19.73

$$C_p \frac{dT}{dt} = QA \exp(-E/RT)f(\alpha) \quad (6)$$

$$\alpha = \int_{T_0}^T \frac{C_p}{Q} dT \quad (7)$$

where C_p is the specific heat capacity (J mol⁻¹ K⁻¹), T is the absolute temperature (K), t is the adiabatic time-to-explosion (s), Q is the exothermic values (J mol⁻¹), A is the pre-exponential factor (s⁻¹), E is the apparent activation energy of the thermal decomposition reaction (J mol⁻¹), R is the gas constant (J mol⁻¹ K⁻¹), $f(\alpha)$ is the most probable kinetic model function and α is the conversion degree.

After integrating of Eq. (6), the adiabatic time-to-explosion equation can be obtained as:

$$t = \int_0^t dt = \int_{T_0}^T \frac{C_p \exp(E/RT)}{QAf(\alpha)} dT \quad (8)$$

where the limit of the temperature integration is from T_0 to T_b .

In fact, the conversion degree (α) of energetic materials from the beginning thermal decomposition to thermal explosion in the adiabatic conditions is very small, and the most probable kinetic model function [$f(\alpha)$] at the process is very difficult to be got. So, Power-low model [Eq. (9)], Reaction-order model [Eq. (10)] and Avrami-Erofeev model [Eq. (11)] were separately used to estimate the adiabatic time-to-explosion, and different rate orders (n) were also supposed.^{29,34} The calculation results were listed in Table 6.

$$f(\alpha) = n\alpha^{(n-1)/n} \quad (9)$$

$$f(\alpha) = (1-\alpha)^n \quad (10)$$

$$f(\alpha) = n(1-\alpha)[- \ln(1-\alpha)]^{(n-1)/n} \quad (11)$$

From Table 6, It can be seen that the calculation results exist in some deviation and the decomposition model has big influence on the adiabatic time-to-explosion. Form the

Table 6. The calculation results of adiabatic time-to-explosion

Equation	Rate order	Model	Time/s
Eq. (15)	$n=1$	$f(\alpha) = 1$	20.14
	$n=2$	$f(\alpha) = 2\alpha^{1/2}$	59.04
	$n=3$	$f(\alpha) = 3\alpha^{2/3}$	70.97
	$n=4$	$f(\alpha) = 4\alpha^{3/4}$	71.47
Eq. (16)	$n=0$	$f(\alpha) = 1$	20.14
	$n=2$	$f(\alpha) = (1-\alpha)^2$	21.37
Eq. (17)	$n=1$	$f(\alpha) = 1-\alpha$	20.75
	$n=2$	$f(\alpha) = 2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	60.36
	$n=3$	$f(\alpha) = 3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	72.37
	$n=4$	$f(\alpha) = 4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	72.80

whole results, the adiabatic time-to-explosion of G(AHDNE) should be a certain value between 60 and 72 s, according to our research experiences. It is a relatively short time, and can be proved credible according to the intense change of DSC curves.

Estimating of Detonation Properties. The empirical Kamlet-Jacobs (K-J) equation is widely applied to estimate the values of detonation velocity (D) and detonation pressure (P) for the explosives only containing C, H, O and N.³⁵⁻³⁷

$$D = 0.7063(NM^{0.5}Q^{0.5})^{0.5}(1 + 1.30\rho) \quad (12)$$

$$P = 0.7619NM^{0.5}Q^{0.5}\rho^2 \quad (13)$$

where D is the detonation velocity (km s⁻¹), P is the detonation pressure (GPa), N is the moles of gases detonation products per gram of explosive, M is the average molecular weight of gaseous products (g mol⁻¹), Q is the chemical energy of detonation (J g⁻¹) and ρ is the density of explosives (g cm⁻³).

D and P of energetic materials can also be predicted with the nitrogen equivalent equation shown as formulas (24)-(26),³⁸ which don't need the value of heat of formation (HOF).

$$\Sigma N = 100\Sigma x_i N_i / M \quad (14)$$

$$D = (690 + 1160\rho) \Sigma N \quad (15)$$

$$P = 1.092(\rho\Sigma N)^2 - 0.574 \quad (16)$$

where ρ is the density of an explosive (g cm⁻³), ΣN is the nitrogen equivalent of the detonation products, N_i is the nitrogen equivalent index of certain detonation product, x_i is the mole number of certain detonation product produced by a mole explosive, M is the formula weight (g mol⁻¹).

From the calculation results, the credible molecular volume is 141.03 cm³ mol⁻¹. So, the theoretical calculation density of G(AHDNE) is 1.58 g cm⁻³, which is close to the single-crystal X-ray densities of G(FOX-7) and G(AHDNE)·H₂O as 1.62 and 1.55 g cm⁻³,^{19,24} indicating the calculation result is credible. The heat of formation (HOF) of G(AHDNE) was also calculated as 83.05 kJ mol⁻¹, according to the semiempirical theoretical calculation. So, the calculated values of D and P for G(AHDNE) were listed in Table 7. From the comparison with other energetic

Table 7. Detonation velocity (D) and detonation pressure (P) of G(AHDNE) and comparison with other energetic materials

Compounds	$D/(\text{km s}^{-1})$	P/GPa
G(AHDNE)	7.3 ^{#1}	22.1 ^{#1}
	7.8 ^{#2}	25.8 ^{#2}
FOX-7	9.0	36.1
RDX	8.7	33.8
TNT	6.8	19.3
NTO	8.7	34.9
AZT	7.6	18.7
GZT	7.1	15.5
BTATz	7.5	22.3
DHT	8.3	30.4

(#1) obtained by K - J equations; (#2) obtained by nitrogen equivalent equations. RDX: 1,3,5-Trinitroperhydro-1,3,5-triazine; TNT: 2,4,6-Trinitrotoluene; NTO: 3-Nitro-1,2,4-triazol-5-one; AZT: N,N -bis-(1H-tetrazol-5-yl) amine salt; GZT: N,N -bis-(1H-tetrazol-5-yl) guanidine salt; BTATz: 3,6-Bis-(1H-tetrazol-5-amino)-1,2,4,5-tetrazine; DHT: 3,6-Dihydrazino-1,2,4,5-tetrazine

materials,^{35,36,39} it can be seen that G(AHDNE) presents good detonation properties.

Conclusions

(1) 1-Amino-1-hydrazino-2,2-dinitroethylene guanidine salt was synthesized. The theoretical investigation on G(AHDNE) was carried out by B3LYP/6-311+G* method. The IR frequencies was performed and compared with the experimental results.

(2) The thermal behaviors of G(AHDNE) present an intense exothermic decomposition process. The enthalpy, apparent activation energy and pre-exponential constant of the decomposition process are -1060 J g^{-1} , $148.7 \text{ kJ mol}^{-1}$ and $10^{15.90} \text{ s}^{-1}$, respectively. The critical temperature of thermal explosion of G(AHDNE) is $152.63 \text{ }^\circ\text{C}$. G(AHDNE) has higher thermal stability than AHDNE.

(3) Specific heat capacity equation of G(AHDNE) is $C_p(\text{J g}^{-1} \text{ K}^{-1}) = -1.1242 + 1.3062 \times 10^{-2} \times T - 1.5229 \times 10^{-5} \times T^2$ ($283.0 \text{ K} < T < 353.0 \text{ K}$), and the molar heat capacity is $314.69 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K . Adiabatic time-to-explosion of G(AHDNE) was calculated to be a certain value between 60-72 s. G(AHDNE) presents good performances.

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