

# Structural Characterization and Thermal Behavior of a Novel Energetic Material: 1-Amino-1-(2,4-dinitrophenylhydrazinyl)-2,2-dinitroethylene

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A novel energetic material, 1-amino-1-(2,4-dinitrophenylhydrazinyl)-2,2-dinitroethylene (APHDNE), was synthesized by the reaction of 1,1-diamino-2,2-dinitroethylene (FOX-7) and 2,4-dinitrophenylhydrazine in *N*-methyl pyrrolidone (NMP) at 110 °C. The theoretical investigation on APHDNE was carried out by B3LYP/6-311+G\* method. The IR frequencies analysis and NMR chemical shifts were performed and compared with the experimental results. The thermal behavior of APHDNE was studied by DSC and TG/DTG methods, and can be divided into two crystal phase transition processes and three exothermic decomposition processes. The enthalpy, apparent activation energy and pre-exponential factor of the first exothermic decomposition reaction were obtained as  $-525.3 \text{ kJ mol}^{-1}$ ,  $276.85 \text{ kJ mol}^{-1}$  and  $10^{26.22} \text{ s}^{-1}$ , respectively. The critical temperature of thermal explosion of APHDNE is 237.7 °C. The specific heat capacity of APHDNE was determined with micro-DSC method and theoretical calculation method, and the molar heat capacity is  $363.67 \text{ J mol}^{-1} \text{ K}^{-1}$  at 298.15 K. The adiabatic time-to-explosion of APHDNE was also calculated to be a certain value between 253.2-309.4 s. APHDNE has higher thermal stability than FOX-7.

**Key Words :** 1-Amino-1-(2,4-dinitrophenylhydrazinyl)-2,2-dinitroethylene (APHDNE), 1,1-Diamino-2,2-dinitroethylene (FOX-7), Theoretical calculation, Thermal behavior, Adiabatic time-to-explosion

## Introduction

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. Since firstly synthesized in 1998,<sup>1,2</sup> FOX-7 has attracted extensive attention and is considered as a promising low-sensitivity ammunition in future. Many researches have been carried out on the synthesis, mechanism, molecule structure, theoretical calculation, thermal behavior, explosive performance and application of FOX-7.<sup>3-28</sup>

FOX-7 is a nitro-enamine belonging to the group of compounds known as "push-pull" alkenes.<sup>29</sup> FOX-7 possesses a highly polarized carbon-carbon double bond, whose positive and negative charges are stabilized by two amino groups and two nitro groups respectively. Therefore, FOX-7 can react with some nucleophiles to form some new energetic compounds. Our interest mainly consisted in modifying molecular structure of FOX-7 in order to obtain new high-energy compounds and study their structure-property relationship.<sup>30-39</sup>

In this paper, we mainly reported the preparation and theoretical calculation of a new derivative of FOX-7, 1-amino-1-(2,4-dinitrophenylhydrazinyl)-2,2-dinitroethylene (APHDNE), studied its thermal behavior with DSC and TG/DTG methods, determined specific heat capacity with micro-DSC method and theoretical calculation method, and calculated adiabatic time-to-explosion for further estimating its thermal stability.

## Experimental

**Preparation of APHDNE.** APHDNE was prepared according to the following method: FOX-7 (0.01 mol, 1.48 g) was dissolved in 12 mL of *N*-methylpyrrolidone (NMP) and to it 2,4-dinitrophenylhydrazine (0.012 mol, 2.38 g) was added drop wise. After reaction at 110 °C for 24 h, the resulting solution was slowly cooled to ambient temperature and diluted with proper amount of water. Many aubergine solid sediments were formed, which were filtered, washed with water, and dried under vacuum, yielding 1.28 g (39.2%). Anal. calcd. for  $\text{C}_8\text{H}_7\text{N}_7\text{O}_8$  (%): C 29.17, H 2.13, N 29.79; found (%): C 28.96, H 2.24, N 30.47. IR (KBr)  $\nu$  3277.5, 3095.9, 1653.1, 1612.9, 1455.0, 1357.4, 1304.6, 1092.6, 931.0  $\text{cm}^{-1}$ . <sup>13</sup>C NMR (DMSO, 400 MHz,  $\delta$ ): 175.23, 144.13, 143.98, 135.33, 127.62, 122.80, 115.07, 105.12 ppm.

**Theoretical Calculation Investigation.** A molecular unit of APHDNE generated from Chem3D software was selected as the initial structure model, while B3LYP/6-311+G\* method in Gaussian 03 package<sup>40</sup> was used to optimize the structure and compute its frequencies at different temperatures and NMR chemical shifts. All convergent precisions are the system default values, and all calculations were carried out on the *Lenovo* computer.

**Experimental Equipments and Conditions.** The DSC experiments for APHDNE were performed using a DSC-Q200 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of  $50 \text{ mL min}^{-1}$  and the amount of used sample was about 1 mg. The heating rates used were 2.5, 5.0, 10.0

and 15.0 °C min<sup>-1</sup> from ambient temperature to 500.0 °C, respectively.

The TG-DTG experiment for APHDNE was performed using a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL min<sup>-1</sup>. The amount of used sample was about 1.5 mg. The heating rate used was 5.0 °C min<sup>-1</sup> from ambient temperature to 500.0 °C.

The specific heat capacity of APHDNE was measured using a Micro-DSCIII apparatus (SETARAM, France) with the sample amount of 277.14 mg. The heating rate was 0.15 °C min<sup>-1</sup> (2.5 × 10<sup>-3</sup> K s<sup>-1</sup>) from 10.0 to 80.0 °C, in which the precisions of temperature and heat flow were 10<sup>-4</sup> °C and 0.2 μW, respectively. The principle for measuring of the continuous specific heat capacity is shown as:

$$C_p = \frac{A_s - A_b}{m_s \times \beta} \quad (1)$$

where  $C_p$  is the specific heat capacity,  $A_s$  and  $A_b$  are the heat flows of the sample and blank,  $m_s$  is the amount of the sample,  $\beta$  is the heating rate.

## Results and Discussion

**The Reaction Mechanism.** FOX-7 is a “push-pull” nitro-enamine and possesses a highly polarized carbon-carbon double bond with positive and negative charges.<sup>6,10-12,29</sup> 2,4-Dinitrophenylhydrazine used as a kind of nucleophile attacks at the positive end of the carbon-carbon double bond, with subsequent replacement of one amino group by one 2,4-dinitrophenylhydrazine group. However, once one of the

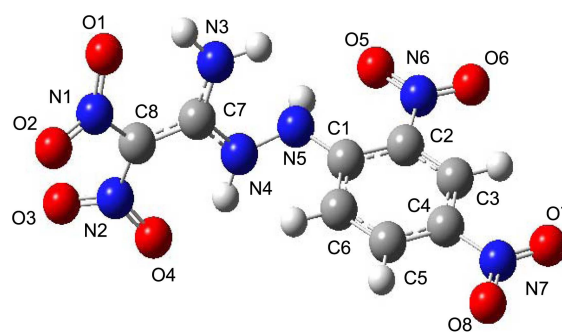


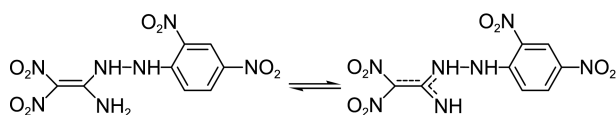
Figure 1. Optimized molecular structure of APHDNE.

two amino groups was substituted by the nucleophile, it was very difficult to replace the other one. The reason for the result should be that (1) the degree of the polarized carbon-carbon double bond was considerably weakened after the first-step replacement reaction, and (2) steric hindrance effect increased. Thus, we only synthesized 1-amino-1-(2,4-dinitrophenylhydrazinyl)-2,2-dinitroethylene (APHDNE), rather than the alternative candidate, 1,1-bis-(2,4-dinitrophenylhydrazinyl)-2,2-dinitroethylene, despite in using different molar proportions of FOX-7 and 2,4-dinitrophenylhydrazine in our experiments.

**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 was stable and calculation results are reliable. Optimized molecular geometry and parameters are shown in

Table 1. Calculated non-hydrogen bond lengths, bond angles and mulliken net charges of APHDNE

Bond length/Å							
N(1)-O(1)	1.247	N(3)-C(7)	1.334	N(6)-C(2)	1.468	C(2)-C(3)	1.393
N(1)-O(2)	1.216	N(4)-C(7)	1.361	N(7)-O(7)	1.224	C(3)-C(4)	1.380
N(1)-C(8)	1.441	N(4)-N(5)	1.382	N(5)-O(8)	1.223	C(4)-C(5)	1.396
N(2)-O(3)	1.215	N(5)-C(1)	1.384	N(7)-C(4)	1.474	C(5)-C(6)	1.380
N(2)-O(4)	1.254	N(6)-O(5)	1.238	C(1)-C(2)	1.422	C(7)-C(8)	1.423
N(2)-C(8)	1.432	N(6)-O(6)	1.217	C(1)-C(6)	1.410		
Bond angles/(°)							
O(1)-N(1)-O(2)	123.2	N(2)-C(8)-C(7)	121.1	C(1)-C(2)-N(6)	122.7	C(4)-N(7)-O(8)	117.1
O(1)-N(1)-C(8)	117.5	N(3)-C(7)-C(8)	122.5	O(5)-N(6)-O(6)	123.6	N(7)-C(4)-C(5)	119.7
O(2)-N(1)-C(8)	119.2	N(3)-C(7)-N(4)	116.9	O(5)-N(6)-C(2)	118.0	C(1)-C(6)-C(5)	121.6
O(3)-N(2)-C(8)	119.8	N(4)-C(7)-C(8)	120.6	O(6)-N(6)-C(2)	118.4	C(6)-C(5)-C(4)	119.5
O(3)-N(2)-O(4)	122.7	N(5)-N(4)-C(7)	120.4	N(6)-C(2)-C(3)	116.3	C(5)-C(4)-C(3)	121.1
O(4)-N(2)-C(8)	117.5	N(4)-N(5)-C(1)	119.2	C(3)-C(4)-N(7)	119.3	C(4)-C(3)-C(2)	119.4
N(1)-C(8)-N(2)	116.6	N(5)-C(1)-C(2)	112.7	O(7)-N(7)-C(4)	117.6	C(3)-C(2)-C(1)	121.2
N(1)-C(8)-C(7)	122.25	N(5)-C(1)-C(6)	120.1	O(7)-N(7)-O(8)	125.3	C(2)-C(1)-C(6)	117.2
Mulliken net charges/e							
C(1)	0.032	C(7)	0.538	N(5)	-0.577	O(4)	-0.145
C(2)	-0.036	C(8)	-0.146	N(6)	-0.247	O(5)	-0.065
C(3)	-0.129	N(1)	-0.195	N(7)	-0.219	O(6)	0.052
C(4)	-0.036	N(2)	-0.165	O(1)	-0.132	O(7)	0.008
C(5)	-0.801	N(3)	-0.776	O(2)	0.052	O(8)	0.001
C(6)	0.624	N(4)	-0.203	O(3)	0.078		



Scheme 1

Figure 1 and Table 1.

Substituting one amino group for one 2,4-dinitrophenylhydrazine group, the molecular symmetry was broken. Molecular space configuration (non-hydrogen atoms) changed greatly from the symmetric plane configuration to the asymmetric three dimensional configurations.<sup>2</sup> The bond length of C(7)-C(8) (1.42 Å) is longer than the average length of C-C double bond (1.32 Å). The bond lengths of N(3)-C(7) and N(4)-C(7) (all equal to 1.34 Å) are shorter than the average length of C-N single bond (1.44 Å), and close to the length of conjugated C-N double bond (1.28 Å). All indicate that the obvious conjugative effect occurs between C(7)-C(8), C(7)-N(3) and C(7)-N(4), and it can be concluded that APHDNE should be the following tautomer structure (conjugated structure) (Scheme 1). From the distribution of atomic net charges, we can see that C(7) atom has more positive charges and C(8) atom presents certain negative charges, indicating that APHDNE is also a typical nitroamine compound and possesses a highly polarized carbon-carbon double bond with positive and negative charges. All corresponding bond lengths and bond angles are in good agreement with these of FOX-7 and its other derivatives.<sup>2,30-34</sup>

On the basis of the simple harmonic oscillator analysis, 84 groups of frequency and intensity were obtained, only those

large than 700  $\text{cm}^{-1}$  are listed in Table 2. The scaled IR frequencies were calibrated by multiplying 0.96. Due to the complexity of vibrational mode, we only analyzed some typical vibrational modes comparing with the experimental data. The theoretical value at 3247  $\text{cm}^{-1}$  caused by the C-H (Benzene) stretching vibration is in agreement with that of the experiment (3096  $\text{cm}^{-1}$ ). The theoretical value at 3525  $\text{cm}^{-1}$  caused by the N-H (-NH<sub>2</sub>) stretching vibration is in agreement with that of the experiment (3277  $\text{cm}^{-1}$ ). The asymmetric and symmetric characteristic absorption peaks of C-N (-NO<sub>2</sub>) are found to be 1112 and 1373  $\text{cm}^{-1}$ , relevant to the experimental values of 1093 and 1357  $\text{cm}^{-1}$ . The theoretical value at 1654  $\text{cm}^{-1}$  caused by the C=C stretching vibration is consistent with that of the experiment (1653  $\text{cm}^{-1}$ ). The absorption peak of the benzene skeleton vibration is found to be at 1442 and 1639  $\text{cm}^{-1}$ , relevant to the experimental values of 1455 and 1653  $\text{cm}^{-1}$ .

Through NMR calculation, we got eight values of the chemical shifts of <sup>13</sup>C, which are listed in Table 3. In comparison with the corresponding experimental data, the calculated results deviate slightly, since the calculation of theoretical properties is based on single gas phase molecule.

**Thermal Behavior.** From the typical DSC and TG/DTG curves (Figs. 2 and 3), we can see that the thermal behavior of APHDNE can be divided into five stages. The first two stages are crystal phase transition processes, and the peak temperatures are 115.37 and 192.37 °C at the heating rate of 5.0 °C min<sup>-1</sup>. The last three stages are the continuous exothermic decomposition processes. The peak temperatures are 244.67, 295.47 and 376.57 °C at the heating rate of 5.0 °C min<sup>-1</sup>, respectively. The thermal behavior was markedly different from that of FOX-7, whose thermal behavior presents only two obvious exothermic decomposition processes, and the peak temperatures of the two processes are 230.1 and 295.5 °C at the heating rate of 10.0 °C min<sup>-1</sup>.<sup>12</sup> We can see that the thermal decomposition temperature and thermal stability of the compound are improved greatly, after reacting with 2,4-dinitrophenylhydrazine. Comparing the result with that of another derivative of FOX-7, 1-amino-1-hydrazino-2,2-dinitroethylene (AHDNE), whose thermal behavior presents two continuous exothermic decomposition processes, and the peak temperatures of the two processes are 113.0 and 133.7 °C at the heating rate of 5.0 °C min<sup>-1</sup>,<sup>32</sup> APHDNE presents much higher thermal stability than

Table 2. Scaled IR frequencies for APHDNE

$\nu/\text{cm}^{-1}$	$I$ /km mol <sup>-1</sup>	Exptl /cm <sup>-1</sup>	$\nu/\text{cm}^{-1}$	$I$ /km mol <sup>-1</sup>	Exptl /cm <sup>-1</sup>
726	19.5		1318	247.1	
730	20.7		1348	176.5	1333
753	18.2		1357	462.9	
756	22.6	766	1373	109.3	1357
776	24.8		1415	39.4	
811	49.6		1442	4.6	1455
848	24.5	841	1483	117.4	
857	22.1		1534	191.0	
864	11.6		1563	533.6	
888	34.8		1578	61.3	
937	38.3		1588	195.5	1584
962	15.3		1602	929.7	
1053	10.4		1609	64.0	1613
1080	62.0		1639	228.4	
1112	35.3	1093	1654	215.1	1653
1146	46.1		1663	344.3	
1161	96.5		3247	24.9	3096
1201	81.1		3442	206.3	
1252	270.9		3515	133.4	3277
1269	241.6		3525	120.9	
1302	147.0	1305	3677	194.1	

Table 3. <sup>13</sup>C NMR chemical shifts

NMR chemical shifts	Calcd/ppm	Exptl/ppm
$\delta$ (C1)	155.50	144.13
$\delta$ (C2)	140.52	127.62
$\delta$ (C3)	130.26	115.07
$\delta$ (C4)	148.95	143.98
$\delta$ (C5)	137.53	122.79
$\delta$ (C6)	117.24	105.12
$\delta$ (C7)	159.30	175.23
$\delta$ (C8)	140.39	135.43

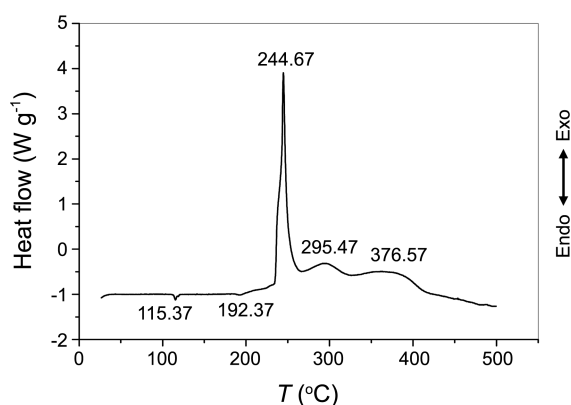


Figure 2. DSC curve of APHDNE at a heating rate of 5.0 °C min<sup>-1</sup>.

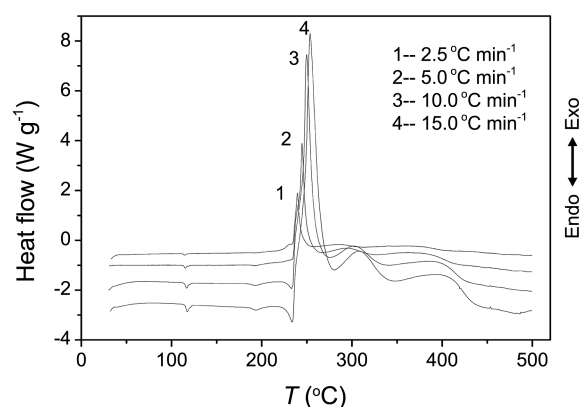


Figure 4. DSC curves of APHDNE at various heating rates.

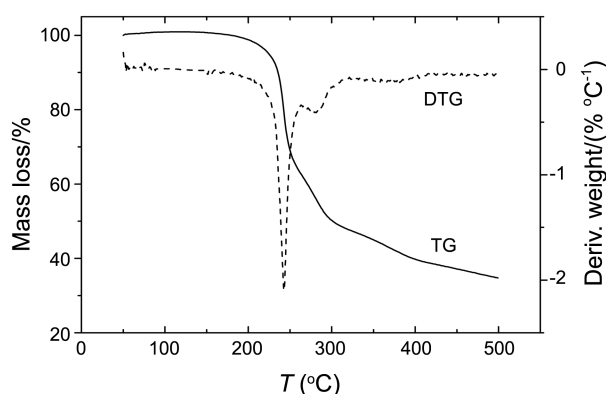


Figure 3. TG-DTG curves of APHDNE at a heating rate of 5.0 °C min<sup>-1</sup>.

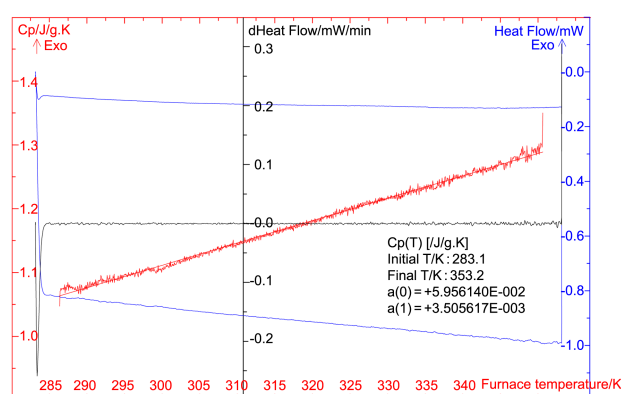


Figure 5. Determination results of the continuous  $C_p$  of APHDNE.

AHDNE. From the above results, we can see that the group behind hydrazine has a great influence on the properties of compound.

In order to obtain the kinetic parameters (the apparent activation energy ( $E$ ) and pre-exponential factor ( $A$ )) of the first exothermic decomposition reaction for APHDNE, a multiple heating method (Kissinger method<sup>41</sup> and Ozawa method<sup>42</sup>) was employed (Fig. 4). The Kissinger and Ozawa equations are as follows:

$$\text{Kissinger Eq.: } \ln\left(\frac{\beta}{T_p^2}\right) = \ln\frac{AR}{E_k} - \frac{E_k}{R T_p} \quad (2)$$

$$\text{Ozawa Eq.: } \log\beta + \frac{0.4567E_0}{RT_p} = C \quad (3)$$

where  $\beta$  is the linear heating rate,  $T_p$  is the peak temperature,  $A$  is the pre-exponential constant,  $R$  is the gas constant,  $E$  is

the apparent activation energy and  $C$  is a constant.

The measured values of the beginning temperature ( $T_0$ ), extrapolated onset temperature ( $T_c$ ), peak temperature ( $T_p$ ) and enthalpy ( $\Delta H_d$ ) of the first exothermic decomposition reaction were listed in Table 4. The values ( $T_{00}$ ,  $T_{e0}$  and  $T_{p0}$ ) of  $T_0$ ,  $T_c$  and  $T_p$  corresponding to  $\beta \rightarrow 0$  obtained by Eq. (4) were also listed in Table 4.<sup>43</sup>

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

where  $n$  and  $m$  are coefficients.

The results obtained by Kissinger and Ozawa methods were listed in Table 5. We can see that the apparent activation energy obtained by Kissinger method agrees well with that by Ozawa method. All the linear correlation coefficients ( $r$ ) are very close to 1. So, the results are credible. Moreover, we can see that the apparent activation energy is higher, which indicates that the thermal stability of APHDNE is good.

Table 4. The values of  $T_0$ ,  $T_c$ ,  $T_p$ ,  $\Delta H_d$ ,  $T_{00}$ ,  $T_{e0}$  and  $T_{p0}$  of the thermal decomposition by DSC curves at various heating rates ( $\beta$ )

$\beta/(\text{°C min}^{-1})$	$T_0/\text{°C}$	$T_c/\text{°C}$	$T_p/\text{°C}$	$\Delta H_d/(\text{kJ mol}^{-1})$	$T_{00}/\text{°C}$	$T_{e0}/\text{°C}$	$T_{p0}/\text{°C}$
2.5	213.58	235.19	239.48				
5.0	217.50	241.15	244.67				
10.0	221.58	244.85	249.68	-525.3	209.84	229.75	235.01
15.0	224.13	245.51	253.62				

**Table 5.** The kinetic parameters obtained by the data in Table 1<sup>a</sup>

$E_k/(kJ mol^{-1})$	$\log(A/s^{-1})$	$r_k$	$E_o/(kJ mol^{-1})$	$r_o$	$\bar{E}/(kJ mol^{-1})$
279.6	26.22	0.9987	274.1	0.9988	276.85

<sup>a</sup>Subscript k, data obtained by Kissinger's method; subscript o, data obtained by Ozawa's method.

The critical temperature of thermal explosion ( $T_b$ ) obtained by Eq. (5)<sup>43</sup> is 237.7 °C, which is higher than that of FOX-7 as 207.1 °C,<sup>12</sup> and AHDNE as 98.2 °C,<sup>32</sup> indicating that APHDNE presents higher thermal stability than FOX-7 and AHDNE.

$$T_b = \frac{E_o - \sqrt{E_o^2 - 4E_oRT_{e0}}}{2R} \quad (5)$$

where  $E_o$  is the value of  $E$  by Ozawa's method.

The entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ) of the first exothermic decomposition stage corresponding to  $T = T_{p0}$  and  $E = E_k$  obtained by Eqs. (6)-(8)<sup>43</sup> are 252.6 J mol<sup>-1</sup> K<sup>-1</sup>, 279.6 kJ mol<sup>-1</sup> and 151.2 kJ mol<sup>-1</sup>, respectively.

$$A = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (6)$$

$$A \exp\left(-\frac{E}{RT}\right) = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (7)$$

$$\Delta S^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (8)$$

where  $k_B$  is the Boltzman constant and  $h$  is the Plank constant.

**Specific Heat Capacity.** Figure 5 shows the determination results of APHDNE using a continuous specific heat capacity mode of Micro-DSCIII apparatus. We can see that the specific heat capacity of APHDNE presents a good linear relationship with temperature in determining temperature range. Specific heat capacity equation is shown as:

$$C_p(J g^{-1} K^{-1}) = 5.9561 \times 10^{-2} + 3.5056 \times 10^{-3}T \quad (9)$$

(283.0 K <  $T$  < 353.0 K)

The molar heat capacity of APHDNE is 363.67 J mol<sup>-1</sup> K<sup>-1</sup> at 298.15 K.

Table 6 shows the results of specific heat capacity by the theoretical calculation and experimental determination and their relative deviations at different temperatures. We can see that the calculated results are all less than the experimental results, and the relative deviations are comparatively great, from 12.88% to 16.46%. This is attributed to single gas phase molecule used in theoretical calculation, which is clearly different to the actual solid phase molecule.

**Thermodynamic Properties.** The enthalpy change, entropy change and Gibbs free energy change of APHDNE were calculated by Eqs. (10)-(12) at 283-353 K, from ambient temperature to thermal decomposition temperature, taking 298.15 K as the benchmark. The results were listed in Table 7.

$$H_T - H_{298.15} = \int_{298.15}^T C_p dT \quad (10)$$

**Table 6.** Results of specific heat capacity by the theoretical calculation and experimental determination and their relative deviation at different temperatures

Temperature /K	$C_p/(J mol^{-1} K^{-1})$		RD /%
	Theoretical calculation value	Experimental value	
283.0	301.61	346.19	12.88
293.0	309.69	357.73	13.43
298.15	313.81	363.67	13.71
303.0	317.66	369.27	13.98
313.0	325.51	380.81	14.52
323.0	333.23	392.35	15.07
333.0	340.82	403.89	15.62
343.0	348.29	415.43	16.16
353.0	355.62	426.97	16.71

**Table 7.** Thermodynamic function data of APHDNE

$T/K$	$H_T - H_{298.15} / (kJ mol^{-1})$	$S_T - S_{298.15} / (J mol^{-1} K^{-1})$	$G_T - G_{298.15} / (kJ mol^{-1})$
283.0	-5.3772	-18.5054	-0.1401
293.0	-1.8576	-6.2847	-0.0162
303.0	1.7774	5.9132	-0.0143
313.0	5.5277	18.0898	-0.1344
323.0	9.3935	30.2463	-0.3761
333.0	13.3746	42.3840	-0.7392
343.0	17.4712	54.5040	-1.2237
353.0	21.6831	66.6074	-1.8293

$$S_T - S_{298.15} = \int_{298.15}^T C_p T^{-1} dT \quad (11)$$

$$G_T - G_{298.15} = \int_{298.15}^T C_p dT - T \int_{298.15}^T C_p T^{-1} dT \quad (12)$$

**Estimation of Adiabatic Time-to-explosion.** Energetic materials need a time from the beginning thermal decomposition to thermal explosion in adiabatic condition. We called the time as the adiabatic time-to-explosion.<sup>35-39,43-47</sup> Ordinarily, we use heating rate ( $dT/dt$ ) and critical heating rate  $(dT/dt)_{T_b}$  in thermal decomposition process to evaluate the thermal stability of energetic materials. However, we can calculate the adiabatic time-to-explosion ( $t$ ) by the following Eqs. (13)-(14)<sup>35-39,44-47</sup> when we have obtained a series of experimental data. Thereby, as an important parameter, it is easy and intuitionistic to evaluate the thermal stability of energetic materials according to the length of the adiabatic time-to-explosion.

$$C_p \frac{dT}{dt} = QA \exp(-E/RT) f(\alpha) \quad (13)$$

$$\alpha = \int_{T_0}^T \frac{C_p}{Q} dT \quad (14)$$

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

According to the above determining results of APHDNE, we use:

$$C_p = a + bT \quad (15)$$

where  $a$  and  $b$  are coefficients.

In fact, the conversion degree ( $\alpha$ ) of energetic materials from the beginning thermal decomposition to thermal explosion in the adiabatic conditions is small, and the most probable kinetic model function [ $f(\alpha)$ ] at this beginning decomposition process is unimportant on the result of the estimation of the adiabatic time-to-explosion. So, we used Eq. (16) and supposed that the rate order of the mechanism function ( $n$ ) of APHDNE in the process equaled 0, 1 and 2.<sup>22,32,33</sup>

$$f(\alpha) = (1-\alpha)^n \quad (16)$$

The combination of Eqs. (13)-(16) gives the following adiabatic time-to-explosion equation:

$$\begin{aligned} t &= \int_0^t dt = \int_{T_0}^T \frac{C_p \exp(E/RT)}{QAf(\alpha)} dT \\ &= \frac{1}{QA} \int_{T_0}^T \frac{(a+bT) \exp(E/RT)}{(1-\alpha)^n} dT \\ &= \frac{1}{QA \left\{ 1 - \frac{1}{Q} \left[ a(T_b - T_{00}) + \frac{b}{2}(T_b^2 - T_{00}^2) \right] \right\}^n} \\ &\quad \int_{T_0}^T (a+bT) \exp(E/RT) dT \end{aligned} \quad (17)$$

The limit of temperature integral in Eq. (17) is from  $T_{00}$  to  $T_b$ . We can directly get  $t_0=253.2$  s,  $t_1=279.9$  s and  $t_2=309.4$  s from Eq. (17), according to the above obtained data. As a rule, the rate order ( $n$ ) of energetic materials ranges from 0 to 2, so the adiabatic time-to-explosion of APHDNE is a certain value between 253.2-309.4 s. The time is much longer than that of FOX-7 as 78.9-88.9 s,<sup>22</sup> and AHDNE as 59.2 s.<sup>32</sup> The sequence of the adiabatic time-to-explosion is well consistent with that of the critical temperature of thermal explosion for the three corresponding compounds. In another aspect, it further proves the higher thermal stability of APHDNE than those of FOX-7 and AHDNE.

### Conclusions

(1) APHDNE was synthesized and theoretical investigation was carried out with B3LYP/6-311+G\* method in Gaussian

03 package. The thermal behavior of APHDNE can be divided into two crystal phase transition processes and three exothermic decomposition processes. The enthalpy, apparent activation energy and pre-exponential factor of the first exothermic decomposition reaction were obtained as  $-525.3$   $\text{kJ mol}^{-1}$ ,  $276.85$   $\text{kJ mol}^{-1}$  and  $10^{26.22}$   $\text{s}^{-1}$ , respectively. The critical temperature of thermal explosion of APHDNE is  $237.7$   $^{\circ}\text{C}$ .

(2) The specific heat capacity of APHDNE was studied. Specific heat capacity equation is  $C_p(\text{J g}^{-1} \text{K}^{-1}) = 5.9561 \times 10^{-2} + 3.5056 \times 10^{-3} T$  ( $283.0$   $\text{K} < T < 353.0$   $\text{K}$ ) and the molar heat capacity is  $363.67$   $\text{J mol}^{-1} \text{K}^{-1}$  at  $298.15$   $\text{K}$ . The adiabatic time-to-explosion of APHDNE was also calculated to be a certain value between 253.2-309.4 s. APHDNE has higher thermal stability than FOX-7 and AHDNE.

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