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新型高能有机钾盐 K(DNDZ)的晶体结构和热行为研究

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摘要:合成了一种新型高能有机钾盐 2-(二硝基亚甲基)-1,3-二氮杂环戊烷钾盐[K(DNDZ)],并培养出单晶。该晶体属单斜晶系,空间群 $P2_1/n$,晶胞参数为:a=0.506 31(19) nm,b=1.336 2(5) nm,c=1.164 9(4) nm,β=99.860(6)°,V=0.776 5(5) nm^3,Z=4,μ=0.674 mm^{-1},F(000)=432,D_c=1.815 g·cm^{-3}。用非等温 DSC 法研究了 K(DNDZ)的热行为,第一放热分解反应的放热焓、表观活化能和指前因子分别为 444.75 kJ·mol^{-1},152.2 kJ·mol^{-1} 和 $10^{13.92}$ s^{-1}。其热爆炸的临界温度为 208.63 ℃。

关键词:1,1-二氨基-2,2-二硝基乙烯(FOX-7);2-(二硝基亚甲基)-1,3-二氮杂环戊烷(DNDZ);晶体结构;热行为
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Structural Characterization and Thermal Behavior of a New High-Energy Organic Potassium Salt: K(DNDZ)

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Abstract: A new high-energy organic potassium salt, 2-(dinitromethylene)-1,3-diazacyclopentane potassium salt [K(DNDZ)], was synthesized and structurally characterized. The crystal belongs to monoclinic system with space group $P2_1/n$ and a=0.506 31(19) nm, b=1.336 2(5) nm, c=1.164 9(4) nm, β=99.860(6)°, V=0.776 5(5) nm^3, Z=4, μ=0.674 mm^{-1}, F(000)=432, and D_c=1.815 g·cm^{-3}. Thermal behavior of K(DNDZ) was studied under the non-isothermal conditions by DSC method. The enthalpy, apparent activation energy and pre-exponential factor of the first exothermic decomposition reaction were 444.75 kJ·mol^{-1}, 152.2 kJ·mol^{-1} and $10^{13.92}$ s^{-1}, respectively. The critical temperature of thermal explosion (T_b) for K(DNDZ) is 208.63 ℃. CCDC: 675360.

Key words: 1,1-diamino-2,2-dinitroethylene (FOX-7); 2-(dinitromethylene)-1,3-diazacyclopentane (DNDZ); crystal structure; thermal behavior

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. When first synthesized in 1998[1], FOX-7 received much attention. Many researches have been carried out on the synthesis, mechanism, molecule structure, thermal behavior, explosive

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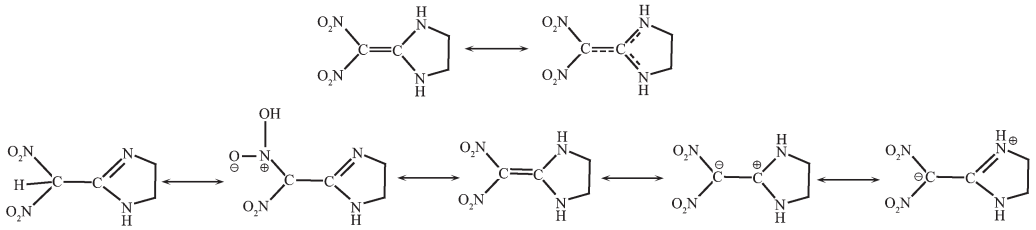
performance and application of FOX-7[2-18].

"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[19]. FOX-7 is a representative "push-pull" nitro-enamine compound. FOX-7 presents certain acidic properties and can react with some nucleophiles to synthesize new high energy derivatives [5,9-11]. 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[20-24].

We prepared a derivative of FOX-7,2-(dinitromethylene)-1,3-diazacyclopentane (DNDZ), and found it still belongs to "push-pull" nitro-enamine compound, has the same characteristics to FOX-7 and exists in manifold tautomers and resonances (Scheme 1)[20]. It can also react with strong alkalis (KOH), and we have used it to prepare a new high-energy organic potassium salt, which will be used as flame suppressor in propellant to substitute inorganic potassium salt (KCl, K_2SO_4, KNO_3 and K_3AlF_6) to generate much more energy and clean gas. In this paper, we reported the crystal structure and thermal behavior of K(DNDZ).



Scheme 1 Tautomers and resonances of DNDZ

1 Experimental

1.1 Sample

K(DNDZ) was prepared as follows: DNDZ (1.74 g) was suspended in 10 mL of water and to it a solution of KOH (1.12 g in 4 mL of water) was added drop wise. After reaction at room temperature for 20 min, 25 mL of methanol were also added drop wise, and the resulting mixture was slowly cooled to 0 ℃. Many bright yellow crystals of K(DNDZ) were formed, which were filtered, washed with methanol and dried under vacuum, yielding 1.51 g (71%). The characteristic peaks of IR (KBr) are: 3 317, 2 972, 2 866, 1 622, 1 511, 1 475, 1 438, 1 361, 1 278, 1 226, 1 097 cm^{-1}. Anal. Calcd.(%) for $C_4H_5N_4O_4K$: C 17.39, H 4.39, N 47.33; found: C 17.46, H 4.38, N 46.63.

1.2 Determination of the single crystal structure

Single crystals suitable for X-ray measurement were obtained by slow evaporation of the above filtrate at room temperature. A bright yellow crystal with dimensions of 0.31 mm×0.18 mm×0.15 mm was chosen for X-ray determination. The data were collected on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm). The structure were solved by the direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were added according to the theoretical models. Crystal data, experimental details and refinement results are summarized in Table 1.

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Table 1 Crystal data and structure refinement details for K(DNDZ)

Chemical formula	$C_4H_5N_4O_4K$	Absorption coefficient / mm^{-1}	0.674
Formula weight	212.22	F(000)	432
Temperature / K	273(2)	θ range / (°)	2.34~25.10
Crystal system	Monoclinic	Index ranges	$-6\leqslant h\leqslant 6$, $-10\leqslant k\leqslant 15$, $-13\leqslant l\leqslant 13$
Space group	$P2_1/n$	Reflections collected	1 370

Continued Table 1

a / nm	0.506 31(19)	Reflections unique (R_{int})	978 (0.003 1)
b / nm	1.336 2(5)	Completeness to θ=27.59° / %	99.90
c / nm	1.164 9(4)	Refinement method	Full-matrix least-squares on F^2
β / (°)	99.860(6)	Goodness-of-fit on F^2	1.004
Volume / nm^3	0.776 5(5)	Final R indices [$I>2\sigma(I)$]	R_1=0.0368, wR_2=0.0850
Z	4	R indices (all data)	R_1=0.052 2, wR_2=0.092 3
D_c / (g·cm^{-3})	1.815	Largest diff. peak and hole / (e·nm^{-3})	346 and −403

1.3 Thermal decomposition condition

The DSC experiments for K(DNDZ) were performed using a DSC-Q200 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 50 mL·min^{-1} and the amount of used sample was about 1 mg. The heating rates used were 2.0, 5.0, 10.0 and 20.0 ℃·min^{-1} from ambient temperature to 500.0 ℃.

2 Results and discussion

2.1 Crystal structure of K(DNDZ)

Selected bond lengths and bond angles of K(DNDZ) are summarized in Table 2. Crystal structure, coordination environments of K^+ and crystal packing of K(DNDZ) are illustrated in Fig.1~3.

Table 2 Selected bond lengths (nm) and bond angles (°) and comparison with DNDZ[20]

			(DNDZ)$^-$	DNDZ		(DNDZ)$^-$	DNDZ
K-O(1)#1	0.276 4	N(1)-O(1)	0.126 4	0.123 1	C(2)-N(4)	0.137 7	0.132 9
K-N(3)#2	0.282 0	N(1)-O(2)	0.124 5	0.121 6	C(3)-N(3)	0.148 7	0.146 4
K-O(4)#3	0.279 4	N(2)-O(3)	0.124 0	0.121 0	C(4)-N(4)	0.147 4	0.145 8
K-N(4)#3	0.315 6	N(2)-O(4)	0.126 1	0.122 8	C(3)-C(4)	0.151 8	0.151 6
K-O(1)#4	0.308 1	N(1)-C(1)	0.137 0	0.140 8			
K-O(2)	0.283 8	N(2)-C(1)	0.138 7	0.140 5			
K-O(2)#4	0.285 8	C(1)-C(2)	0.147 2	0.143 1			
K-O(3)	0.284 8	C(2)-N(3)	0.127 8	0.132 5			

					(DNDZ)$^-$	DNDZ
O(1)#1-K-N(3)#2	83.4	O(4)#3-K-O(3)	109.8	O(1)-N(1)-C(1)	115.9	117.9
O(1)#1-K-O(4)#3	113.7	N(4)#3-K-O(1)#4	104.7	O(2)-N(1)-C(1)	123.8	121.9
O(1)#1-K-N(4)#3	175.3	N(4)#3-K-O(2)	64.1	O(3)-N(2)-C(1)	123.2	122.7
O(1)#1-K-O(1)#4	114.6	N(4)#3-K-O(2)#4	117.1	O(4)-N(2)-C(1)	115.8	117.9
O(1)#1-K-O(2)	75.2	N(4)#3-K-O(3)	82.0	O(1)-N(1)-O(2)	120.2	120.2
O(1)#1-K-O(2)#4	67.5	O(1)#4-K-O(2)	42.9	O(3)-N(2)-O(4)	121.1	119.4
O(1)#1-K-O(3)	102.1	O(1)#4-K-O(2)#4	95.6	N(1)-C(1)-N(2)	121.7	117.9
N(3)#2-K-O(4)#3	87.6	O(1)#4-K-O(3)	64.9	N(1)-C(1)-C(2)	120.7	120.9
N(3)#2-K-N(4)#3	92.0	O(2)-K-O(2)#4	125.5	N(2)-C(1)-C(2)	117.4	121.2
N(3)#2-K-O(1)#4	95.8	O(2)-K-O(3)	73.4	C(1)-C(2)-N(3)	122.5	125.9
N(3)#2-K-O(2)	84.0	O(2)#4-K-O(3)	54.5	C(1)-C(2)-N(4)	120.3	124.8
N(3)#2-K-O(2)#4	144.7			N(3)-C(2)-N(4)	117.1	109.4
N(3)#2-K-O(3)	157.1			C(2)-N(3)-C(3)	105.4	112.4
O(4)#3-K-N(4)#3	66.5			C(2)-N(4)-C(4)	105.6	112.1
O(4)#3-K-O(1)#4	170.8			N(3)-C(3)-C(4)	105.6	102.3
O(4)#3-K-O(2)	129.5			N(4)-C(4)-C(3)	101.0	103.0
O(4)#3-K-O(2)#4	86.4					

Symmetry code: #1: $-x+1, -y, -z+1$; #2: $-x, -y, -z+1$; #3: $-x+1/2, y-1/2, -z+3/2$; #4: $x-1, y, z$.

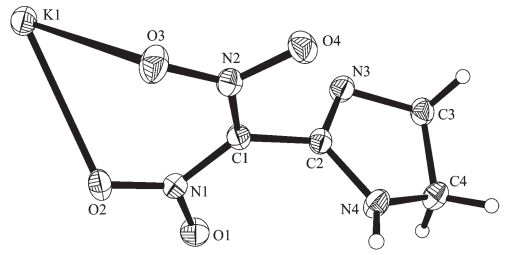
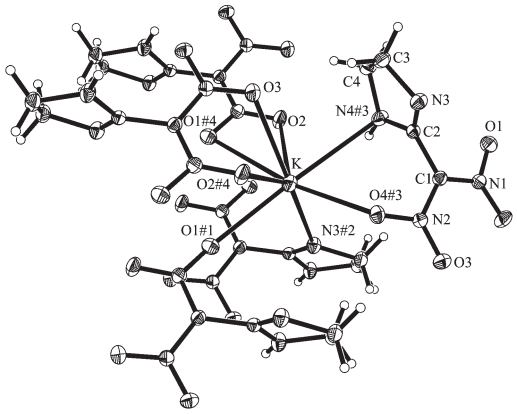


Fig.1 Crystal structure of K(DNDZ), Displacement ellipsoids for all atoms are drawn at the 30% probability level



Symmetry code: #1: $-x+1, -y, -z+1$; #2: $-x, -y, -z+1$; #3: $-x+1/2, y-1/2, -z+3/2$; #4: $x-1, y, z$

Fig.2 Coordination environment of K^+ ion in K(DNDZ)

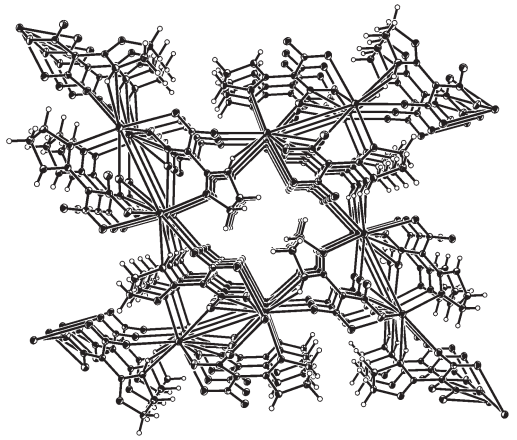
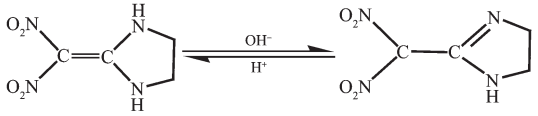


Fig.3 Crystal packing of K(DNDZ)

The crystallographic studies revealed that the compound of K(DNDZ) is made up of K^+ ion and $(DNDZ)^-$ anion (Fig.1). In crystal structure, one K^+ ion is coordinated by five adjacent $(DNDZ)^-$ anions through six K-O [K-O(1)#1 0.276 5 nm, K-O(4)#3 0.279 4 nm, K-O (1)#4 0.308 1 nm, K-O (2) 0.283 8 nm, K-O(2)#4 0.285 8 nm, K-O(3) 0.284 8 nm] and two K-N [K-N(3)#2 0.282 0 nm, K-N(4)#3 0.315 6 nm] interactions (Fig.2). Simultaneity, one $(DNDZ)^-$ anion interacts with five adjacent K^+ ions through the same interactions. All finally expand to the formation of 3D framework of K(DNDZ) (Fig.3).

The space configuration of $(DNDZ)^-$ anion changes from original one plane to two approximate orthogonal planes (all no-hydrogen atoms)[20], and the intersection of the two approximate orthogonal planes is C(1)-C(2) bond. From Table 2, we can see that many selected bond lengths and bond angles changed greatly after DNDZ became $(DNDZ)^-$ by reaction. The symmetrical and approximately equal bond lengths and bond angles in DNDZ was not consistent with each other through different coordination interactions with K^+ ion. Theoretical C(1)-C(2) double bond (0.147 3 nm) in $(DNDZ)^-$ was closer to C-C single bond (0.153 nm) than that in DNDZ. Equilong C(2)-N(3) and C(2)-N(4) bonds presented big deviation (0.127 8 and 0.137 7 nm). C(2)-N(3) in $(DNDZ)^-$ has already been typical C-N double bond. DNDZ has changed into its one tautomer format (Scheme 2). So, we can conclude the molecular space configuration of DNDZ can be changed and circumvolve around C(1)-C(2) bond according to existent surroundings, further indicating DNDZ exists in manifold tautomers.



Scheme 2

2.2 Thermal behavior of K(DNDZ)

The typical DSC curve (Fig.4) indicates that K(DNDZ) has no melting point, and its thermal behavior can be divided into two obvious exothermic decomposition stages. The first stage occurs at 180~240 ℃, and the extrapolated onset temperature, peak temperature and decomposition enthalpy are 220.43 ℃, 227.72 ℃ and 1 832.5 $J \cdot g^{-1}$ at the heating rate of 10.0 $℃ \cdot min^{-1}$, respectively. The second stage occurs at 240~350 ℃, and the extrapolated onset temperature, peak temperature and enthalpy are 316.83 ℃, 327.89 ℃ and 637.13 $J \cdot g^{-1}$ at the heating rate of 10.0 $℃ \cdot min^{-1}$, respectively. But, there is still a very unconspicuous crystal phase transition process. The peak temperature and enthalpy

of the crystal phase transition are 131.45 ℃ and 1.923 J·g^{-1} at the heating rate of 2.5 ℃·min^{-1}. All are very different from that of DNDZ whose thermal behavior presents only one intense exothermic decomposition process, and the extrapolated onset temperature and peak temperature are 256.64 and 267.60 ℃ at the heating rate of 10.0 ℃·min^{-1} [20]. K(DNDZ) presents lower thermal stability than DNDZ.

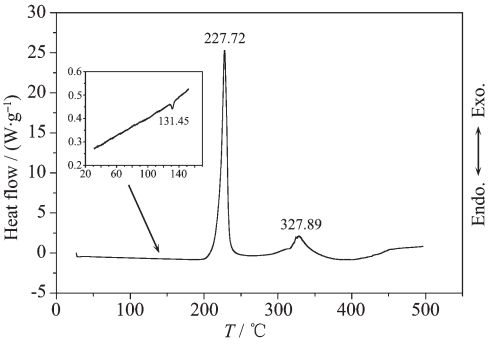


Fig.4　DSC curve of K(DNDZ) at the heating rate of 10.0 ℃·min^{-1}

A multiple heating method (Kissinger method[25] and Ozawa method[26]) was employed to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential factor (A)) of the first exothermic decomposition reaction of K(DNDZ).

The Kissinger and Ozawa equations are as follows:

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

$$\lg\beta+\frac{0.456\,7E}{RT_p}=C \quad (2)$$

where β 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 extrapolated onset temperature (T_e), and peak temperature (T_p) of the first exothermic decomposition reaction were listed in Table 3. The above-mentioned values (E and A) determined by Kissinger method and Ozawa method and linear correlation coefficients (r) are also listed in Table 3.

Table 3　Values of T_e and T_p at various heating rates and the kinetic parameters in the first exothermic stage

β / (℃·min^{-1})	T_e / ℃	T_p / ℃	E_k / (kJ·mol^{-1})	lgA_k / s^{-1}	r_k	E_o / (kJ·mol^{-1})	r_o	$\bar{E}$ / (kJ·mol^{-1})
2.5	203.13	211.39	152.0	13.92	0.998 5	152.4	0.998 7	152.2
5.0	211.76	219.26						
10.0	220.43	227.72						
20.0	229.31	238.17						

Subscript k, data obtained by Kissinger's method; subscript o, data obtained by Ozawa's method.

From the results, we can see that the apparent activation energy obtained by Kissinger method agrees well with that obtained by Ozawa method, moreover, the linear correlation coefficients (r) are all very close to 1. So, the result is credible. Moreover, the apparent activation energy (E) of the first exothermic decomposition reaction was lower, indicating that K (DNDZ) is easy to decompose at temperature above 180 ℃.

The value of T_{e0} in the first exothermic decomposition stage corresponding to $\beta\to0$ obtained by Eq.(**3**) is 195.95 ℃[27].

$$T_{ei}=T_{e0}+n\beta_i+m\beta_i^2 \qquad i=1\sim4 \quad (3)$$

where n and m are coefficients.

The critical temperature of thermal explosion (T_b) obtained by Eq.(**4**) was 208.63 ℃[27], which is lower than that of DNDZ as 261.04 ℃[20].

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

where E_O is the value of the apparent activation energy obtained by Ozawa's method.

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