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Crystal structure of 3,4-dinitropyrazole in water

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ABSTRACT

3,4-dinitropyrazole (DNP) was synthesized by N-nitration, thermal rearrangement and C-nitration with pyrazole as the raw material. A pure DNP single crystal was obtained by solvent evaporation using water as a solvent, and its structure was characterized by X-ray single crystal diffraction. The results showed that the single crystal structure of DNP contained water, and the molar ratio of DNP/water was 4:1. The DNP molecules existed stably due to the presence of intermolecular and intramolecular hydrogen bonding, as well as π-π stacking between DNP molecules. This study was valuable to the production and application of DNP.

KEYWORDS

DNP; melt-casting explosives carrier; crystal water; hydrogen bond

1. Introduction

Improving energy and safety is an eternal theme for the development of explosive technology. The explosive should meet the requirements of high energy and insensitivity when charging. At present, 90% of the melt-casting explosives use TNT as a liquid carrier. However, TNT has the disadvantages of oil impregnate, contraction and expansion during melt-casting [1], and the pollutants will pose a serious threat to the environment. Therefore, searching a new generation of high-energy insensitive melting cast explosive carrier with superior performance as well as environmentally friendly technology to replace TNT has become a hot spot.

Nitrogen heterocyclic energetic compounds contain high electronegative nitrogen and oxygen atoms, as well as, high nitrogen contents. The presence of π-electron system makes nitrogen heterocyclic compounds have the advantages of insensitivity, high enthalpy of formation, high density, good thermal stability and environmental friendliness [2]. DNP is an outstanding representative of nitrogen heterocyclic energetic compounds, which has a broad prospect in melt-casting explosives carrier [3]. David et al. [4] reported a series of properties of DNP such as melting point and detonation speed, and it was shown that the performance was superior than that of TNT (Table 1).

Refining the crude DNP with water to remove residual acid can reduce cost and environmental pollution. However, the collected DNP solid particles will melt when

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Table 1. The properties of TNT and DNP.

Materials	Density (g/cm^3)	Melting point (°C)	Detonation speed (m/s)	Explosive pressure (Gpa)	Explosive heat (kJ/kg)	Oxygen balance (%)	Energy density (kJ/cm^3)
TNT	1.65	80.9	6900	21	3335	−74	6.997
DNP	1.87	85	8108	29.4	–	−25.48	8.211

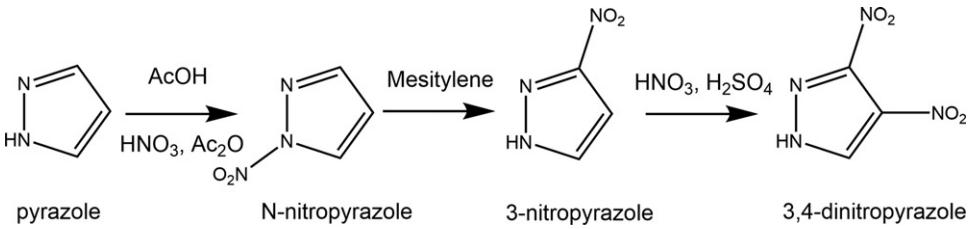

Figure 1. The synthetic route of DNP.

dried, which indicates that DNP contains a large amount of water. Therefore, it is necessary to explore the crystal form of DNP, the hydrogen bond network of DNP molecules and water molecules, as well as the type of water in DNP (crystal water or free water).

In this study, DNP was synthesized via N-nitration, thermal rearrangement and C-nitration. DNP crystal was obtained via water evaporation, and its crystal structure was analyzed by X-ray single crystal diffraction and further compared with those grown in different solvents.

2. Experimental Section

2.1. Materials

Pyrazole was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd.; Acetic acid and nitric acid (98%) were purchased from Tianjin Chemical Reagent Research Institute; Sulfuric acid was purchased from Beijing Lianhua Yongxing Technology Development Co., Ltd.; Acetic anhydride, sodium chloride and ether were purchased from Sinopharm Chemical Reagent Co., Ltd.; Phenylacetonitrile and petroleum ether were purchased from Tianjin Beichen Fangzheng Reagent Factory; Deionized water was prepared from laboratory. All reagents used were of analytic grade.

2.2. Synthesis of DNP

The process for synthesizing 3,4-dinitropyrazole (DNP) can be divided into three steps including N-nitration, thermal rearrangement and C-nitration. The synthetic route is presented in Figure 1.

Pyrazole was selected as the starting material [5], to which, nitric acid (98%) and acetic anhydride were added. The N-nitration reaction was carried out at room temperature for 30 min. With N-nitropyrazole in hand, thermal rearrangement was proceeded at a reaction temperature of 438.15 K and a reaction time of 30 min using

mesitylene as a solvent to obtain 3-nitropyrazole, after which, added with nitric acid and sulfuric acid. C-nitration reaction was carried out at 375.15 K for 30 min, affording 3,4-dinitropyrazole. The transparent crystal of DNP was obtained by slow evaporation from deionized water at room temperature.

2.3. Instrumentation

X-ray single crystal diffraction of DNP was recorded on a Bruker APEX-II CCD Diffractometer. The crystal was kept at 220.0 K during data collection. Using Olex2 [6], the structure was solved with the ShelXT [7] structure solution program using Intrinsic Phasing and refined with the ShelXL [8] refinement package using Least Squares minimization.

Melting point of DNP crystallized in different solvents including ether, benzene and water was measured by BUCHI M-565 Melting Point Meter (Switzerland). The temperature was ranging from 50 to 100 °C, with a heating rate of 2 °C/min.

The impact sensitivity of DNP was determined by its explosion probability, using a calibrated Type 12 Vertical Drop Hammer, with a drop weight of 2.5 kg and a drop height of 80 cm. Experiment was carried out at an ambient temperature of 25 °C and a relative humidity of 35%. A total of 25 same samples was selected, and each sample was 35 mg. The explosion probability was calculated by Eq (1).

$$P = \frac{X}{25} \times 100\% \tag{1}$$

Where P is the explosion probability, X is the number of explosion in 25 experiments.

3. Results and Discussion

3.1. Crystal Structure of DNP

The crystal and instrumental parameters used in the unit cell determination together with the data collection and structure refinement parameters are shown in Table 2.

DNP crystal was a yellow, transparent and uniform bulk substance, and its molecular structure is shown in Figure 2.

The structure of crystal was symmetrical, and the ratio of DNP/water was 4:1. The oxygen atom of the water molecule located on a twofold axis, and the occupancy factor of the water molecule was 0.5. It can be founded that the pyrazole parent ring was planar, and there were 5 atoms in the least-squares plane (C1, C2, C3, N3, N4; C4, C5, C6, N8, N7). The dihedral angle between plane 1 (C1, C2, C3, N3, N4) and two nitro groups were 15.402° (O2, N1, O1) and 32.217° (O3, N2, O4), respectively. The dihedral angle between plane 2 (C4, C5, C6, N7, N8) and two nitro groups were 17.522° (O7, N5, O8) and 25.288° (O5, N6, O6), respectively. In addition, the dihedral angle of the plane in which two DNP molecules located was 17.378°. Furthermore, water molecules and DNP molecules were connected by hydrogen bonds, and the ratio was 1:4.

The network of hydrogen bonds and the specific information regarding the hydrogen bond of DNP crystal are shown in Figure 3 and Table 3, respectively.

Table 2. Crystal data and structure refinement parameters of DNP.

Item	Value
Empirical formula	$C_{12}H_{10}N_{16}O_{17}$
Formula weight	650.36
Temperature/K	220.0
Crystal system	monoclinic
Space group	P2/n
a/Å	11.5494(18)
b/Å	7.1894(11)
c/Å	15.166(2)
α/°	90
β/°	99.843(3)
γ/°	90
Volume/Å^3	1240.7(3)
Z	2
ρ_{calc}g/cm^3	1.741
μ/mm^{-1}	0.163
F (000)	660.0
Crystal size/mm^3	0.28 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.112 to 53
Index ranges	$-14 \leq h \leq 14$ $-8 \leq k \leq 8$, $-19 \leq l \leq 18$
Reflections collected	6832
Independent reflections	2507 [R_{int}= 0.0231, R_{sigma}= 0.0304]
Data/restraints/parameters	2507/2/216
Goodness-of-fit on F^2	1.126
Final R indexes [I> =2σ (I)]	R_1= 0.0389, wR_2= 0.1157
Final R indexes [all data]	R_1= 0.0451, wR_2= 0.1211
Largest diff. peak/hole / e Å^{-3}	0.34/-0.26

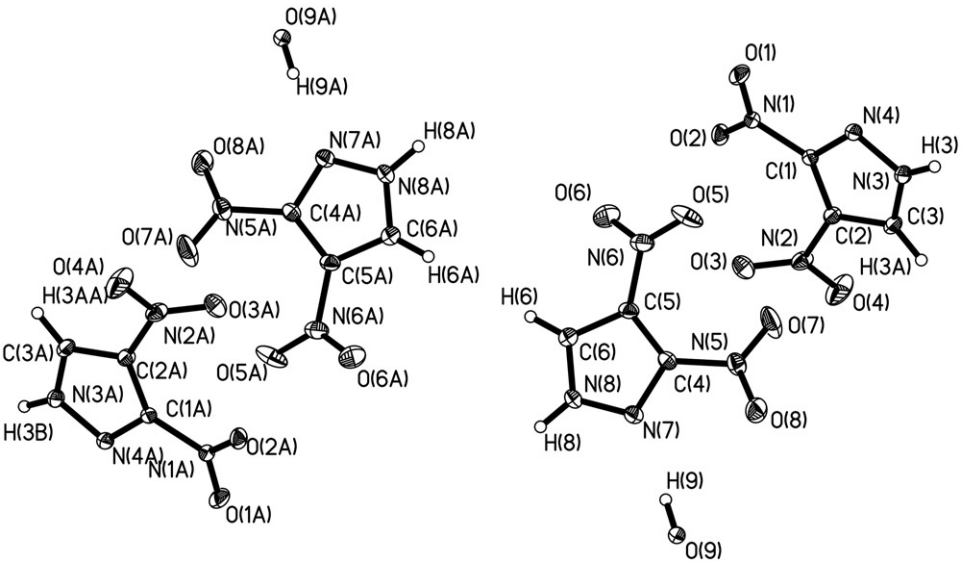

Figure 2. The molecular structure of DNP.

From Table 3, it can be concluded that there are intermolecular hydrogen bonds (N-H···N and C-H···O) and intramolecular hydrogen bonds between DNP molecules, as well as, intermolecular hydrogen bonds (O-H···N) between DNP molecules and water molecules. Due to the action of hydrogen bond, the stability and security of DNP can be improved.

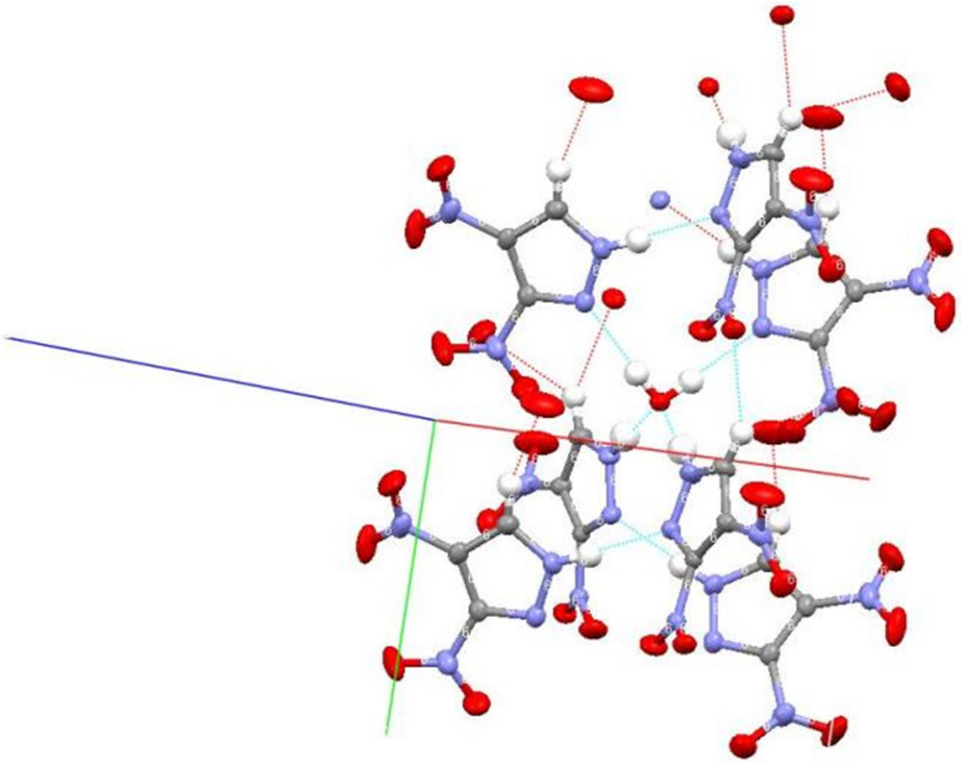

Figure 3. The network of hydrogen bonds.

Table 3. The length and angle of hydrogen bond.

D-H···A	d(D-H)/Å	d(H···A)/Å	d(D···A)/Å	d(D···A)/Å
N(3)-H(3)···O(9)#1	0.886	1.923	2.787	174.32
N(8)-H(8)···N(4)#2	0.887	2.082	2.964	172.51
O(9)-H(9)···N(7)#3	0.860	2.055	2.913	175.97
C(3)-H(3A)···O(2)#3	0.940	2.505	3.353	150.08
C(3)-H(3A)···O(6)#3	0.940	2.565	3.293	134.55
C(6)-H(6)···O(4)#5	0.940	2.565	3.326	155.99

#1: 1-x, 2-y, 1-z; #2: 1/2 + x, 1-y, -1/2 + z; #3: x, 1 + y, z; #5: x, 1 + y, z.

3.2. Comparison of Crystal Structure of DNP Crystallized in Different Solvents

As shown in Table 4, there is little difference in the crystal system, bond length and bond angle of DNP grown in different solvents, on the contrary, the space group, density and dihedral angle between nitro plane and pyrazole mother-ring plane of DNP vary with the solvent. It can be founded that the space group of DNP crystals containing no solvent molecules was $P2_1/c$, and that of containing water and benzene were P2/n and $P2_1/n$ respectively. The crystal density of the solvent-free DNP was greater than 1.8 g/cm^3, and that of the solvent-containing DNP was less than 1.8 g/cm^3. The presence of solvent molecules reduced the crystal density. In addition, for those DNP crystals containing no solvent molecules, the dihedral angle between the plane of the nitro group crystal and pyrazole ring was greater than 40°, and those solvent-containing DNP crystals showed an opposite result, which is due to the action of the hydrogen bond between the solvent molecule and the DNP molecule.

Table 4. Crystal structure of DNP crystallized in different solvents.

Solvent	Ether	Ether	Ether	Benzene	Water
Formula	$C_3H_2N_4O_4$	$C_3H_2N_4O_4$	$C_3H_2N_4O_4$	$2C_3H_2N_4O_4{\cdot}0.5C_6H_6$	$4C_3H_2N_4O_4{\cdot}H_2O$
FW [g/mol]	158.09	158	158.09	355.23	650.36
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	P2/n
Size [mm]		$0.47 \times 0.45 \times 0.41$		$0.40 \times 0.30 \times 0.15$	
$0.10 \times 0.22 \times 0.28$		$0.30 \times 0.20 \times 0.20$		$0.28 \times 0.15 \times 0.12$	Color/Habit
Light yellow block	Colourless block	Light yellow block	Colourless block	Colourless block	
a [Å]	9.9801 (8)	9.7013 (13)	9.8326 (4)	7.4579 (15)	11.5494 (18)
b [Å]	11.9959 (9)	12.0797 (10)	12.0559 (4)	9.787 (2)	7.1894 (11)
c [Å]	9.7192 (7)	9.7587 (7)	9.7190 (4)	19.534 (4)	15.166 (2)
α [°]	90	90	90	90	90
β [°]	94.232 (1)	93.962 (11)	93.959 (4)	94.87 (3)	99.843 (3)
γ [°]	90	90	90	90	90
V [Å^3]	1160.41 (15)	1140.88 (19)	1149.35 (8)	1420.7 (5)	1240.7 (3)
λMoKα [Å]	0.71	0.71073	0.71073	0.71073	0.71073
Z	8	8	8	4	2
Dataset h; k; l	−11–11; 14–10; −10–11	–	−12–12; −12–14; −11–11	−9–9; −12–1; −25–25	−14–14; −8–8; −19–18
ρ [g/cm^{-3}]	1.80969	1.84	1.827	1.661	1.741
R_1 (obs)	0.1012	0.0408	0.0324	0.060	0.0389
wR_2 (all data)	0.1377	0.1001	0.0930	0.105	0.1211
S	–	–	1.04	0.92	1.126
T [K]	298	105.3	123	123	220
F (000)	640	–	640	724	660
μ [mm^{-1}]	–	0.17	0.17	0.15	0.163
Ref.	[9]	[10]	[11]	[12]	**This study**

Table 5. Melting point of DNP crystallized in different solvents.

Solvent	Water	Benzene	Ether
Melting Point	87.3	88.2	87.7

Table 6. The explosion probability of DNP crystallized in different solvents.

	1	2	3	4	5	6	7	8	9	10	11	12	13
Water	×	×	×	×	×	×	×	×	×	×	×	×	×
Benzene	×	×	×	×	○	×	×	○	×	×	×	×	×
Ether	×	×	×	×	×	×	×	○	×	×	×	×	×

	14	15	16	17	18	19	20	21	22	23	24	25
Water	×	×	×	×	×	×	×	×	×	×	×	×
Benzene	×	○	×	×	×	×	×	×	×	×	×	×
Ether	×	×	×	×	×	×	×	○	×	×	×	×

3.3. Comparison of Melting Point of DNP Crystallized in Different Solvents

Table 5 compares the melting point of DNP crystallized in water, benzene and ether. The melting points of DNP crystal crystallized in different reagents were different, which indicated that the properties of crystal were influenced by solvent.

3.4. Comparison of Impact Sensitivity of DNP Crystallized in Different Solvents

From Table 6, the number of explosion for the sample crystallized in water, benzene and ether is 0, 3 and 2, respectively. Therefore, the explosion probability of DNP

crystallized in three different solvents was different, namely, benzene (12%) > ether (8%) > water (0%). The dihedral angle between the nitro and pyrazole plane was different, and the impact sensitivity of DNP was directly influenced by the dihedral angle. Therefore, water can be determined as an excellent solvent for recrystallization of DNP.

4. Conclusions

In this study, DNP was synthesized by N-nitration, thermal rearrangement and C-nitration using pyrazole as the raw material, and its single crystal was obtained by solvent evaporation using water as solvent. X-ray single crystal diffraction confirmed that the single crystal structure of DNP contained water, which can be removed by melt-drying. Through the analysis of hydrogen bond of DNP, the stability and security of DNP can be improved owing to the presence of intermolecular and intramolecular hydrogen bonds. Furthermore, it was founded that the crystal system, bond length and bond angle of DNP crystal grown in different solvents were same, and the space group, dihedral angle, melting point and impact sensitivity were influenced by solvent. Water is a promising solvent for recrystallization of DNP due to its environmental friendliness and low-cost, and the properties of DNP recrystallized in water were all in line with the standards. This study is of great significance to the production and application of DNP.

Disclosure statement

No potential conflict of interest was reported by the authors.

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