Wang Jianlong*, Liu Yunzhang, Chen Lizhen, Li Zhihua and Hu Wanghua

The crystal structure of the solid solution of 3,5-dinitropyrazole and 4-chlorine-3,5-dinitropyrazole, $C_3H_{1.24}Cl_{0.76}N_4O_4$

Table 1: Data collection and handling.

Crystal:	Yellow sheet
Size:	$0.27 \times 0.22 \times 0.06$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.46 mm^{-1}
Diffractometer, scan mode:	PHOTON 100 CMOS, ω
θ_{max} , completeness:	25.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	3726, 1194, 0.039
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 936
$N(\text{param})_{\text{refined}}$:	113
Programs:	Bruker [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1997(2)	0.1477(4)	0.7225(3)	0.0176(6)
C3	0.2318(2)	−0.1557(4)	0.8410(3)	0.0189(6)
N1	0.11605(19)	−0.1325(4)	0.7972(2)	0.0203(5)
H1	0.058(2)	−0.219(5)	0.810(3)	0.024*
N2	0.09410(18)	0.0545(3)	0.7249(2)	0.0204(5)
N3	0.20633(19)	0.3560(4)	0.6490(2)	0.0224(5)
N4	0.2731(2)	−0.3457(4)	0.9217(2)	0.0251(5)
O1	0.11465(17)	0.4387(3)	0.5932(2)	0.0330(5)
O2	0.30479(17)	0.4400(3)	0.6473(2)	0.0337(5)
O3	0.19906(19)	−0.4917(3)	0.93913(19)	0.0344(5)
O4	0.37760(18)	−0.3525(4)	0.9667(2)	0.0413(6)
C2 ^a	0.2921(2)	0.0257(4)	0.7952(3)	0.0195(6)
Cl1 ^a	0.43231(8)	0.08109(18)	0.82221(11)	0.0389(4)
C2 ^b	0.2921(2)	0.0257(4)	0.7952(3)	0.0195(6)
H2 ^b	0.3742	0.0589	0.8092	0.023*

^aOccupancy: 0.749(4), ^bOccupancy: 0.251(4).

<https://doi.org/10.1515/ncrs-2019-0345>

Received May 17, 2019; accepted July 18, 2019; available online September 11, 2019

Abstract

$C_3H_{1.24}Cl_{0.76}N_4O_4$, monoclinic, $P2_1/c$ (no. 14), $a = 11.3953(11)$ Å, $b = 5.9373(4)$ Å, $c = 9.7498(9)$ Å, $\beta = 96.630(4)^\circ$, $V = 655.23(10)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0446$, $wR_{\text{ref}}(F^2) = 0.1068$, $T = 173(2)$ K.

CCDC no.: 1941444

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

An amount of 2 g of recrystallized 4-chloro-3,5-dinitropyrazole was placed in a hydrothermal reaction vessel

*Corresponding author: Wang Jianlong, School of Chemical Engineering and Technology, North University of China, Taiyuan 030051, Shanxi Province, P.R. China, e-mail: 619379961@qq.com

Liu Yunzhang and Chen Lizhen: School of Chemical Engineering and Technology, North University of China, Taiyuan 030051, Shanxi Province, P.R. China

Li Zhihua and Hu Wanghua: Gansu Yinguang Chemical Industry Group Co. LTD, China North Industries, Group Corporation Limited, Baiyin 730900, Gansu Province, P.R. China

(80 mL), 25 mL of ammonia water was added thereto, and the reaction kettle was tightly sealed and placed in a vacuum drying oven. The temperature is slowly raised to 160 °C, reaction 8 h, and after the reaction is finished, it is naturally cooled to room temperature; Take out the reactor and pour the orange solid-liquid mixture in the reactor into a four-port bottle of 100 mL. The temperature was raised to 70 °C with stirring, and the pH of the solution was adjusted to 1 with 10% hydrochloric acid. At this time, the solution turned pale yellow; when the temperature was lowered to room temperature, a yellow solid was precipitated, and a yellow solid and a

yellow filtrate were obtained by filtration, and the filtrate was evaporated at room temperature to obtain a yellow crystal suitable for single crystal X-ray diffraction. This crystal contains 3,5-dinitropyrazole and 4-chlorine-3,5-dinitropyrazole in the ratio 1/3 (Table 2).

Experimental details

All H atoms were identified in difference Fourier syntheses. With C—H bond lengths constrained to 0.95° and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, N—H bond 0.86° and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$.

Comment

Nitropyrazole compounds have high nitrogen content, high enthalpy of formation, high density, low sensitivity and environment-friendly characteristics, and have become a research hotspot in the field of energy-containing materials in recent years [4–6]. 4-Amino-3,5-dinitropyrazole (LLM-116) is one of the high-energy and insensitive compounds with excellent performance and low sensitivity, which has potential application prospects in insensitive explosives [7, 8]. In order to study the mechanism of synthesis of LLM-116, the title compound was prepared by the nitration of 4-chloro-3,5-dinitropyrazole. Here we reproduce the structure of the title compound (the figure).

As shown in the figure, the crystal structure of the title compound was analyzed and refined using the SHELXL program [1–3]. In the crystal structure of the title compound, 4-chloro-3,5-dinitropyrazole forms a solid solution with 3,5-dinitropyrazole. All bond lengths and angles are substantially the same as those of 4-chloro-3,5-dinitropyrazole, but in the crystal structure, the crystal structure of the title compound appears in a rectangular parallelepiped shape with a certain inclination, and the single crystal structure of 4-chloro-3,5-dinitropyrazole exhibits a square shape [9]. And compared with the crystal structure of 3,5-dinitropyrazole [10], the structure has a certain degree of tilt, and the bond

angle and bond length between the atoms also have a certain change [11, 12].

Acknowledgements: We thank the Center of Testing and Analysis, Beijing University of Chemical Technology, for support.

References

1. BRUKER. SAINT, APEX2 and SADABS. Bruker AXS Inc., Madison, WI, USA (2014).
2. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
3. Sheldrick, G. M.: SHELXT-integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
4. Dalinger, I. L.; Popova, G. P.; Vatsadze, I. A.: Synthesis of 3,4,5-trinitropyrazole. *Russ. Chem. Bull.* **108** (2009) 2185–2185.
5. Wang, Y.; Zhao, F.; Ji, Y.: Synthesis and thermal behaviors of 4-amino-3,5-dinitro-1H-pyrazole. *J. Anal. Appl. Pyrolysis* **98** (2012) 231–235.
6. Wu, J.; Cao, D.; Wang, J.; Liu, Y.; Li, Y.: Progress on 3,4,5-trinitro-1H-pyrazole and its derivatives. *Chin. J. Energ. Mater.* **24** (2016) 1121–1130.
7. Qiao, R.; Wang, Y.; Li, Y.: One-pot synthesis of 4-chloro-3,5-dinitropyrazole. *Chem. Int.* **4** (2014) 42–44.
8. Wang, B.; Wang, Y.; Zhang, Z.; Xiong, C.; Zhang, Y.: Synthesis and characterization of 4-amino-3,5-dinitropyrazole (LLM-116) condensation products. *Chin. J. Energ. Mater.* **17** (2009) 293–295.
9. Fischer, D.; Gottfried, J. L.; Klapötke, T. M.; Karaghiosoff, K.; Stierstorfer, J.; Witkowski, T. G.: Synthesis and investigation of advanced energetic materials based on bispyrazolylmethanes. *Angew. Chem. Int. Ed.* **55** (2016) 16132–16135.
10. Wang, Y.; Ji, Y.; Wang, B.; Zhao, F.; Chen, B.; Wei, T.: Crystal structure analysis of 3,5 dinitropyrazole. *Chem. Propel. Polym. Mater.* **12** (2014) 87–89.
11. Bolter, M. F.; Harter, A.; Klapötke, T. M.; Stierstorfer, J.: Isomers of dinitropyrazoles: synthesis, comparison and tuning of their physicochemical properties. *ChemPlusChem* **55** (2018) 804–811.
12. Chen, L.; Song, L.; Cao, D.; Wang, J.: Crystal structure of 3,4-dinitropyrazole, C₃H₂N₄O₄. *Z. Kristallogr. NCS* **231** (2016) 1099–1100.