Xue Mei, Xiang Yong, Wang Jian, Zhang Yushan, Yao Yuehua and Wang Jianlong*

The crystal structure of 3-chloro-1-hydrazino-2,4,6-trinitrobenzene, $C_6H_4ClN_5O_6$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.08 × 0.06 × 0.04 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.43 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	26.4°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7003, 1974, 0.070
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1268
$N(\text{param})_{\text{refined}}$:	171
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.61771(8)	0.79091(15)	0.50526(5)	0.0355(3)
O1	0.9015(2)	0.6515(5)	0.55432(14)	0.0455(7)
O2	0.9138(2)	0.2714(5)	0.56408(14)	0.0475(7)
O3	0.7745(2)	−0.1102(4)	0.31743(15)	0.0432(7)
O4	0.5901(2)	−0.0182(4)	0.22709(13)	0.0365(6)
O5	0.3144(2)	0.5900(4)	0.35412(14)	0.0421(7)
O6	0.4257(2)	0.9114(4)	0.34942(14)	0.0358(6)
N1	0.8632(3)	0.4537(5)	0.53113(16)	0.0335(7)
N2	0.6758(3)	0.0201(5)	0.29058(17)	0.0308(7)
N3	0.4650(3)	0.3801(5)	0.23775(15)	0.0309(7)
H3	0.459213	0.254406	0.207780	0.037*
N4	0.3823(3)	0.5769(5)	0.20935(18)	0.0349(7)
N5	0.4178(3)	0.6978(5)	0.35429(16)	0.0291(6)
C1	0.7524(3)	0.4303(5)	0.45836(18)	0.0253(7)
C2	0.7578(3)	0.2478(5)	0.40926(18)	0.0263(7)
H2	0.829735	0.136294	0.424932	0.032*
C3	0.6611(3)	0.2220(5)	0.33753(18)	0.0232(7)
C4	0.5519(3)	0.3844(5)	0.30993(18)	0.0237(7)
C5	0.5443(3)	0.5575(5)	0.36709(18)	0.0238(7)
C6	0.6411(3)	0.5870(5)	0.43848(18)	0.0250(7)
H4A	0.303(3)	0.529(5)	0.1891(19)	0.027(9)*
H4B	0.417(4)	0.658(7)	0.174(2)	0.063(13)*

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Abstract

$C_6H_4ClN_5O_6$, monoclinic, $P2_1/n$ (no. 14), $a = 10.2139(13)$ Å, $b = 5.6835(6)$ Å, $c = 17.597(2)$ Å, $\beta = 106.484(4)^\circ$, $V = 979.6(2)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0497$, $wR_{\text{ref}}(F^2) = 0.1138$, $T = 173$ K.

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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.

*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

Xue Mei, Zhang Yushan and Yao Yuehua: School of Chemical Engineering and Technology, North University of China, Taiyuan 030051, Shanxi Province, P.R. China. <https://orcid.org/0000-0002-2210-5124> (X. Mei)

Xiang Yong: Sichuan North Hongguang Special Chemical Co., Ltd., Yibin 644104, Sichuan Province, P.R. China

Wang Jian: No. 113, Tianjin Road, Jianxi District, Luoyang 471003, Henan Province, P.R. China

Source of material

2,4-Dichloro-1,3,5-trinitrobenzene was reacted with an appropriate amount of hydrazine hydrate at room temperature for half an hour. After filtering and drying, the crude product

was obtained and purified by column chromatography to give the title compound. Yellow crystals were obtained by slowly evaporating an ethyl acetate solution at room temperature.

Experimental details

C2- and N3-bound H2 and H6 atoms were placed geometrically and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$. The N4-bound H-atoms were located from difference Fourier maps and their positions and isotropic temperature factors freely refined.

Comment

Nitrophenyl hydrazine derivatives have broad applications in the fields of medicinal and materials chemistry; they can be used as test reagents for carbonyl groups and as intermediates for the synthesis of pharmaceuticals [5–9].

In the crystal structure of the title compound all bond lengths and angles are within normal ranges and in good agreement with those found for the structure of 2,4,6-trinitrophenylhydrazine [10] and 1,3-dichloro-2,4,6-trinitrobenzene [11]. The structure of the title compound (cf. the figure) has one benzene ring, and three nitro groups, one hydrazine group and one chlorine as substituents. The dihedral angles between the nitro groups and the benzene ring are 36.89(17), 4.24(17) and 65.73(17)° for the nitro groups at N1, N2 and N5, respectively. The dihedral angle between the hydrazine group and the benzene ring is 15.8(17)° (N4, N3, C4). The hydrazine group donates a total of four hydrogen bonds, including an intramolecular one: N3–H3···O4 [N3···O4 = 2.632(44) Å with angle at H3 = 127], N3–H3···O2ⁱ [N3···O2ⁱ = 3.074(4) Å with angle at H3 = 129 for (i) $-1/2 + x, 1/2 - y, -1/2 + z$]; N4–H4a···O6ⁱⁱ [N4···O6ⁱⁱ = 3.163(4) Å with angle at H4a = 171(3)° for (ii) $1/2 - x, -1/2 + y, 1/2 - z$] and N4–H4b···O1ⁱⁱⁱ [N4···O1ⁱⁱⁱ = 3.189(4) Å with angle at H4b = 154(3)° for (iii) $-1/2 + x, 3/2 - y, -1/2 + z$].

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