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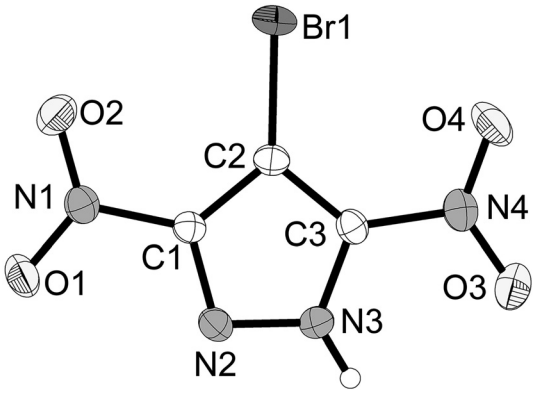
The crystal structure of 4–bromo-3,5-dinitropyrazole



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Abstract

$C_3HBrN_4O_4$, monoclinic, $P2_1/c$ (no. 14), a = 11.9791(4) Å, b = 5.9291(2) Å, c = 9.8188(4) Å, β = 96.520(1)°, V = 692.87(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0291, $wR_{ref}(F^2)$ = 0.0676, T = 170 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.12 × 0.08 × 0.05 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	5.91 mm^{-1}
Diffractometer, scan mode:	Bruker D8 VENTURE, φ and ω
θ_{max}, completeness:	26.4°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5,904, 1,420, 0.062
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1,217
$N(param)_{refined}$:	113
Programs:	Olex2,[1] SHELX[2,3]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	0.42789 (2)	0.59901 (5)	0.32996 (3)	0.03578 (14)
C1	0.1891 (2)	0.6482 (4)	0.2241 (2)	0.0184 (6)
C2	0.2777 (2)	0.5308 (4)	0.2979 (3)	0.0197 (5)
C3	0.2215 (2)	0.3468 (4)	0.3433 (2)	0.0199 (6)
H3	0.058 (2)	0.276 (4)	0.314 (3)	0.030 (9)*
N1	0.1930 (2)	0.8572 (4)	0.1491 (2)	0.0233 (5)
N2	0.0898 (2)	0.5511 (4)	0.2249 (2)	0.0217 (5)
N3	0.1117 (2)	0.3642 (4)	0.2984 (2)	0.0226 (5)
N4	0.2602 (2)	0.1563 (4)	0.4263 (2)	0.0248 (5)
O1	0.10506 (19)	0.9310 (3)	0.0912 (2)	0.0335 (5)
O2	0.28446 (19)	0.9499 (3)	0.1491 (2)	0.0336 (5)
O3	0.18942 (19)	0.0096 (3)	0.4399 (2)	0.0322 (5)
O4	0.35761 (19)	0.1525 (3)	0.4761 (2)	0.0374 (5)

1 Source of material

Add 25 ml of 95 % concentrated sulfuric acid to a four necked flask, maintain the temperature at 0–10 °C, and slowly add 4-bromopyrazole in batches to completely dissolve it. Then continue to maintain the temperature at 0–10 °C, measure 20 ml of fuming nitric acid and put it into the drip funnel, adjust the knob to make it drip slowly, and the drip is completed in about 40 min. After the dropwise addition is complete, use an oil bath to raise the temperature to 100 °C and track it with thin layer chromatography (using ethyl acetate as the developing agent). Stop the reaction and cool it to room temperature after the raw material point completely disappears. Pour the reaction solution into crushed ice. After all the ice is melted, a white precipitate is precipitated, filtered and dried. The filtrate is extracted multiple times with ether or ethyl acetate, and the filtered and extracted products are combined to obtain crystals through solvent evaporation.

2 Experimental details

The N3–H3 bond length was constrained to 0.87 Å with sigma of 0.02.

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3 Comment

The molecular structure of the pyrazole ring is relatively stable, and other functional groups can be introduced. If two or more nitro groups are attached to the three carbon atoms of the pyrazole ring, it will increase the energy density of the compound and reduce sensitivity, thereby improving the overall performance of the compound.[4–6] Nitrification reaction is an important and widely studied chemical reaction.[7] This study used 4-bromopyrazole as the raw material and obtained an important intermediate for the preparation of its high-energy insensitive derivative through nitration reaction.

From the figure, it can be seen that the nitro groups in the crystal structure of 4-bromo-3,5-dinitropyrazole are respectively connected to C(1) and C(3) of the pyrazole ring, while bromine is connected to C(2) of the pyrazole ring. Br(1), N(1), and N(4) atoms are coplanar with the pyrazole ring molecule. Bonding parameters are all in the expected ranges.[8]

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Conflict of interest: The authors declare no conflicts of interest regarding this article.

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