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The cocrystal structure of 4-nitropyrazole – acetic acid (1/1), C₅H₇N₃O₄

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Abstract

C₅H₇N₃O₄, monoclinic, $P\bar{1}$ (no. 2), $a = 5.1166(12)$ Å, $b = 8.711(2)$ Å, $c = 8.744(2)$ Å, $\alpha = 103.169(7)^\circ$, $\beta = 90.454(6)^\circ$, $\gamma = 96.121(7)^\circ$, $V = 377.08(16)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0619$, $wR_{\text{ref}}(F^2) = 0.1241$, $T = 173(2)$ 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.

Source of material

An amount of 25.9 mL of acetic anhydride was added to a 100 mL four-necked flask, cooled in an ice water bath, and 13.8 g of 3-nitropyrazole was slowly added to the reaction flask in batches, stirred for 10 min, then 7.8 mL of fuming nitric acid was slowly added dropwise. After the addition is completed, the system is heated to 50 °C, and the reaction is carried out at a constant temperature for 4 h. After the

Table 1: Data collection and handling.

Crystal:	Colourless column
Size:	0.40 × 0.22 × 0.17 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.13 mm ⁻¹
Diffractometer, scan mode:	PHOTON 100 CMOS, ω
θ_{max} , completeness:	25.4°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	2798, 1365, 0.078
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 785
$N(\text{param})_{\text{refined}}$:	116
Programs:	Bruker [1], Olex2 [2], SHELX [3]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1955(6)	0.2210(4)	0.1159(4)	0.0223(9)
H1	0.3414	0.1743	0.1461	0.027*
C2	0.0827(6)	0.1964(4)	−0.0322(4)	0.0167(8)
C3	−0.1250(6)	0.2883(4)	−0.0188(4)	0.0194(8)
H3	−0.2397	0.2937	−0.1030	0.023*
C4	0.6237(7)	0.6508(4)	0.4093(4)	0.0209(8)
C5	0.4688(7)	0.7787(4)	0.4881(4)	0.0320(11)
H5A	0.3375	0.7364	0.5532	0.048*
H5B	0.3798	0.8198	0.4087	0.048*
H5C	0.5865	0.8646	0.5545	0.048*
N1	−0.1395(5)	0.3670(3)	0.1281(3)	0.0248(8)
N2	0.0572(6)	0.3237(3)	0.2077(3)	0.0227(8)
H2A	0.090(6)	0.358(4)	0.309(2)	0.027*
N3	0.1625(6)	0.0923(3)	−0.1706(3)	0.0240(8)
O1	0.3596(5)	0.0259(3)	−0.1604(3)	0.0364(8)
O2	0.0302(5)	0.0748(3)	−0.2926(3)	0.0337(7)
O3	0.5665(5)	0.6010(3)	0.2557(3)	0.0256(7)
H3B	0.663(6)	0.534(3)	0.221(4)	0.031*
O4	0.7883(5)	0.5931(3)	0.4721(3)	0.0280(7)

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reaction is completed, the reaction solution is poured into 200 g of ice water to precipitate a large amount of white solid, and the filtrate is evaporated at room temperature to obtain colourless crystals.

Experimental details

All H atoms were identified in difference Fourier syntheses. With C–H bond lengths constrained to 0.95° and

$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the hydrogen atoms of pyrazole ring, C—H bond 0.98° and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl group, N—H bond 0.874° 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]. 3,4,5-Trinitro-1*H*-pyrazole (TNP) is widely studied because it is the only pyrazole compound with full carbon nitrification. TNP and its derivatives can be widely used in pesticide, medicine, dye, energy-containing materials and other fields, which has far-reaching research significance and broad development prospects [7, 8]. In order to study the synthesis mechanism of TNP, the title compound was prepared by nitrification reaction of 3-nitropyrazole, which was slowly added into acetic anhydride cooled by ice bath giving a cocrystal.

In the crystal structure of the title compound, 4-nitropyrazole molecules exist in pairs with acetic acid molecules, forming a cocrystal structure. 4-Nitropyrazole molecule is often used as a ligand to form coordination compounds with certain molecules [9, 10], and the cocrystal structure of the title compound is also relevant. The bond angle between the atoms in the 4-nitropyrazole molecule some what different from the bond angle between the atoms in the 4-nitropyrazole single crystal, which may be due to the presence of the acetic acid molecule and the corresponding hydrogen bond [11]. By $\text{NH}\cdots\text{O}$ and $\text{OH}\cdots\text{N}$ hydrogen bonds two acid molecules and two pyrazole molecules are linked to a ring.

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