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Crystal structure of 1–methyl-3-propyl-4-nitro-1H-pyrazole-5-carboxylic acid, $C_8H_{11}N_3O_4$

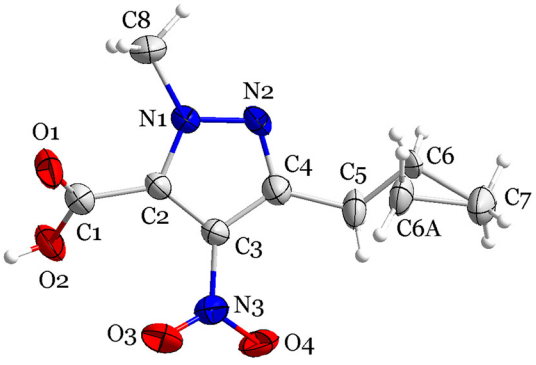
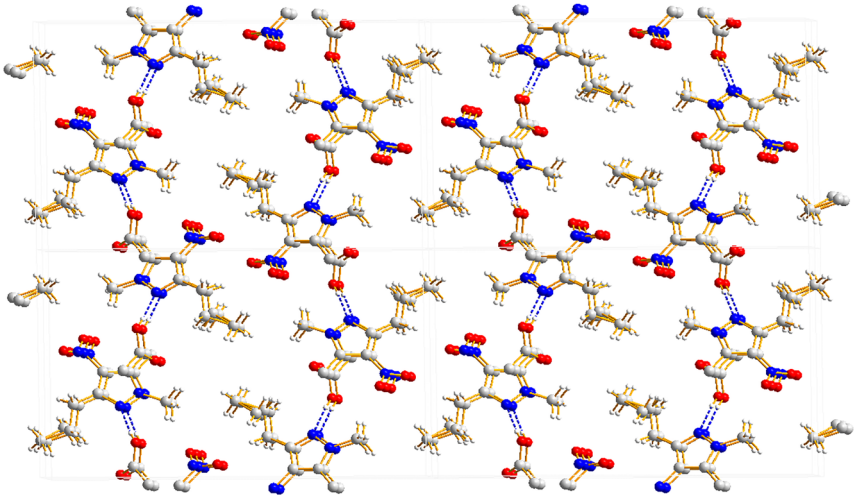


Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.23 × 0.17 × 0.15 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7790, 1955, 0.046
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1221
$N(param)_{refined}$:	153
Programs:	Bruker,[1] SHELX,[2,3] Diamond[4]



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Abstract

[$C_8H_{11}N_3O_4$], monoclinic, $P2_1/c$ (no. 14), a = 4.5811(16) Å, b = 19.734(7) Å, c = 11.812(4) Å, β = 101.181(11)°, V = 1047.6(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0742, $wR_{ref}(F^2)$ = 0.1176, T = 296(2) K.

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

1 Source of materials

To a stirred solution of 65 % concentrated nitric acid (120 mL) and 98 % concentrated sulfuric acid (180 mL) was added 1-methyl-3-propyl-1H-pyrazole-5-carboxylic acid (38.62 g, 0.23 mol). After heated at 100 °C for 16 h, the reaction was completed (monitored by TLC). The reaction solution was

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	1.3410 (6)	0.29653 (15)	0.5133 (2)	0.1072 (10)
O2	1.1428 (5)	0.25361 (12)	0.65278 (19)	0.0834 (8)
H2	1.2933	0.2682	0.6947	0.100*
O3	1.2302 (7)	0.11401 (14)	0.6067 (2)	0.1158 (11)
O4	0.8442 (7)	0.05339 (15)	0.5592 (3)	0.1226 (12)
N1	0.7795 (5)	0.24700 (12)	0.3729 (2)	0.0588 (7)
N2	0.5908 (6)	0.20091 (13)	0.3140 (2)	0.0657 (8)
N3	0.9850 (8)	0.10356 (14)	0.5508 (2)	0.0730 (8)
C1	1.1680 (8)	0.26039 (16)	0.5468 (3)	0.0620 (9)
C2	0.9445 (6)	0.21973 (14)	0.4667 (2)	0.0513 (7)
C3	0.8591 (7)	0.15316 (14)	0.4669 (2)	0.0541 (8)
C4	0.6380 (7)	0.14301 (16)	0.3702 (3)	0.0621 (9)
C5	0.4728 (10)	0.0812 (2)	0.3225 (3)	0.0988 (14)
H5A	0.6046	0.0431	0.3457	0.119*
H5B	0.3079	0.0763	0.3624	0.119*
C6[a]	0.357 (6)	0.0728 (9)	0.2066 (14)	0.098 (7)
H6A[a]	0.4739	0.0995	0.1626	0.118*
H6B[a]	0.1557	0.0904	0.1904	0.118*
C7	0.3516 (12)	−0.0017 (2)	0.1644 (4)	0.146 (2)
H7A	0.2733	−0.0273	0.2205	0.175*
H7B	0.1920	0.0151	0.1076	0.175*
H7C	0.4746	−0.0301	0.1286	0.175*
C8	0.7637 (8)	0.31731 (15)	0.3345 (3)	0.0776 (11)
H8A	0.9562	0.3317	0.3233	0.116*
H8B	0.7015	0.3454	0.3919	0.116*
H8C	0.6229	0.3212	0.2632	0.116*
C6A[b]	0.560 (4)	0.0547 (5)	0.2206 (10)	0.100 (4)
H6AA[b]	0.597 (13)	0.080 (3)	0.154 (4)	0.149*
H6AB[b]	0.754 (8)	0.040 (3)	0.262 (5)	0.149*

[a]Occupancy: 0.35(2), [b]Occupancy: 0.65(2).

poured into ice water (200 mL), and the white precipitate appeared. The solid precipitate was collected by vacuum filtration and crystallized from acetone to obtain 1-methyl-4-nitro-3-propyl-1H-pyrazole-5-carboxylic acid in 79.6 % yield. ^{1}H (400 MHz)and ^{13}C (100 MHz) NMR spectra of 1-methyl-4-nitro-3-propyl-1H-pyrazole-5-carboxylic acid were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) and $CDCl_3$ (^{13}C, δ 77.0 ppm) as internal standards. *J*-values were given in Hertz. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.99–1.03 (t, J = 8.0 Hz, 3H, CH_2CH_3), 1.68–1.77 (m, 2H, CH_2CH_3), 2.86–2.90 (t, J = 8.0 Hz, 2H, CH_2C=N), 4.14 (s, 3H, N–CH_3), 8.38 (br, 1 H, COOH) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 158.58, 149.81, 132.33, 130.87, 40.63, 29.08, 21.25, 13.79 ppm.

2 Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C–H = 0.90–0.97 Å with U_{iso}(H) = 1.5 U_{eq}(C) for methyl H atoms and 1.2 U_{eq}(C) for all other H atoms.

3 Comment

Having been developed by Pfizer and first come into the market in the United States in April 1998, Sildenafil (trade name: Viagra) is a highly selective and specific phosphodiesterase type 5 inhibitor (PDE5i) to treat erectile dysfunction (ED),[5,6] to protect the heart and lungs to enhance the vitality of the body, to treat pulmonary hypertension,[7–9] and to promote left ventricular function and cardiopulmonary performance.[10,11] Nowadays, the synthesis and modification of Sildenafil have also attracted wide attention from chemical workers. Recently, an impactful and high-yielding method for the synthesis of Sildenafil has been developed in our group, and single crystals of several key intermediates have been achieved, and the using of the key intermediates as catalytic agents has been also explored.

In the molecule of the title compound bond lengths and angles within 1-methyl-3-propyl-4-nitro-1H-pyrazole-5-carboxylic acid are very similar to those given in the literature.[12–14] The propyl group in the molecule is disordered. The dihedral angles between the pyrazole ring, the O1–C1–O2 carboxyl group and the nitro group are 48.8°, 21.3° and 52.239(364)°, respectively. The torsion angles of C3–C4–C5–C6, C3–C4–C5–C6A, C4–C5–C6–C7 and C4–C5–C6A–C7 are –151.9°, –106.3°, 148.2° and –171.0°, respectively. Intermolecular O–H···N hydrogen bonds between oxygen atom (O2) of carboxyl group and nitrogen atoms (N2) of pyrazole ring connect the adjacent title compound to form a one dimensional chain. In addition, there also exist weak Intermolecular C–H···O hydrogen bonds, which contributes to the stability of the crystal structure.

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

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