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1-Methyl-3-propyl-1*H*-pyrazole-5-carboxylic acid

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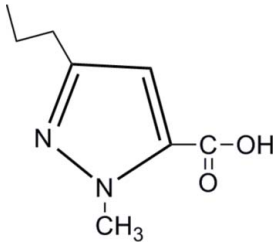
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.004 Å; R factor = 0.054; wR factor = 0.157; data-to-parameter ratio = 13.9.

In the title compound, $C_8H_{12}N_2O_2$, an intermediate in the synthesis of sidenafil, the crystal packing is consolidated by O—H···N and C—H···O interactions.

Related literature

For synthesis, see: Bell *et al.* (1992).



Experimental

Crystal data

$C_8H_{12}N_2O_2$
M_r = 168.20
Monoclinic, $P2_1/c$
a = 4.9336 (19) Å
b = 19.121 (7) Å
c = 9.568 (4) Å
β = 92.136 (7)°
V = 902.0 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 294 (2) K
0.50 × 0.20 × 0.10 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.948, T_{max} = 0.991
4542 measured reflections
1585 independent reflections
1090 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.157
S = 1.03
1585 reflections
114 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N2^{i}	0.84 (3)	1.88 (3)	2.712 (3)	169 (3)
C5—H5A···O2^{ii}	0.97	2.48	3.430 (4)	166

Symmetry codes: (i) $x+1, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x-1, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2523).

References

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supplementary materials

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1-Methyl-3-propyl-1*H*-pyrazole-5-carboxylic acid

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Comment

Sidenafil has been found to be particularly useful in the treatment of inter alia, male erectile dysfunction. The structure of the title compound, (I), (Fig. 1) a key intermediate in the synthesis of sidenafil, is reported here.

As shown in Fig. 2, the packing is consolidated by a conbination of O—H···N and C—H···O interactions (Table 1) resulting in molecular chains propagating in [20$\bar{1}$].

Experimental

The title compound was prepared according to the method of Bell *et al.* (1992). 1-Methyl-3-propyl-1*H*-pyrazole-5-carboxylic acid ethyl ester (20.2 g, 0.10 mol) was suspended in 6 N aqueous sodium hydroxide solution (50 ml, 0.30 mol). The mixture was heated to 353 K for 2 h then diluted with water (50 ml) and acidified with concentrated hydrochloric acid (25 ml). Filtration gave the carboxylic acid as pale brown crystals (12.3 g, 71%), m.p. 423–427 K. Colourless blocks of (I) suitable for X-ray analysis were obtained by slow evaporation of a methanol/ethyl acetate mixture (1:1 *v*/*v*).

Refinement

The O-bound H atom was located in a difference map·Its position was freely refined, with U_{iso}(H) = 1.5U_{eq}(O). The C-bound H atoms were positioned geometrically (C—H = 0.93–0.97 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Figures

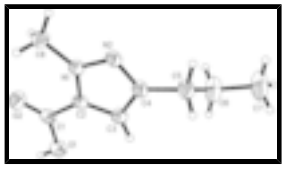

Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

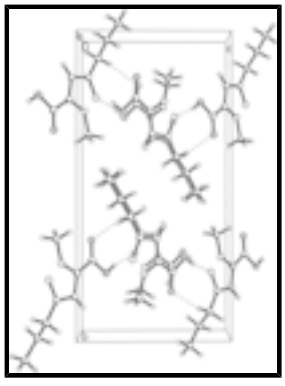

Fig. 2. The crystal packing for (I), with O—H···N and C—H···O interactions shown as dashed lines.

1-Methyl-3-propyl-1*H*-pyrazole-5-carboxylic acid

Crystal data

$C_8H_{12}N_2O_2$	F_{000} = 360
M_r = 168.20	D_x = 1.239 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 1522 reflections
a = 4.9336 (19) Å	θ = 2.4–26.3º
b = 19.121 (7) Å	μ = 0.09 mm^{-1}
c = 9.568 (4) Å	T = 294 (2) K
β = 92.136 (7)º	Block, colourless
V = 902.0 (6) Å^3	0.50 × 0.20 × 0.10 mm
Z = 4	

Data collection

Bruker SMART 1000 CCD diffractometer	1585 independent reflections
Radiation source: fine-focus sealed tube	1090 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.038
T = 294(2) K	θ_{max} = 25.0º
ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	h = −5→5
T_{min} = 0.948, T_{max} = 0.991	k = −11→22
4542 measured reflections	l = −11→11

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difmap and geom
$R[F^2 > 2\sigma(F^2)]$ = 0.054	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.157	$w = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 0.3462P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(\Delta/\sigma)_{max}$ = 0.004
1585 reflections	$\Delta\rho_{max}$ = 0.26 e Å^{-3}
114 parameters	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.7756 (3)	0.22535 (10)	−0.19643 (18)	0.0556 (6)
H1	0.887 (7)	0.2471 (16)	−0.245 (3)	0.083*
O2	0.6976 (4)	0.33056 (10)	−0.1072 (2)	0.0638 (6)
N1	0.2945 (4)	0.26597 (10)	0.06131 (19)	0.0405 (5)
N2	0.1416 (4)	0.21980 (10)	0.1296 (2)	0.0448 (5)
C1	0.6546 (5)	0.26908 (13)	−0.1126 (2)	0.0434 (6)
C2	0.4590 (4)	0.23211 (12)	−0.0261 (2)	0.0394 (6)
C3	0.4085 (5)	0.16227 (12)	−0.0133 (2)	0.0458 (6)
H3	0.4905	0.1260	−0.0607	0.055*
C4	0.2087 (5)	0.15646 (12)	0.0855 (2)	0.0452 (6)
C5	0.0766 (5)	0.09284 (13)	0.1413 (3)	0.0594 (8)
H5A	−0.0493	0.1070	0.2115	0.071*
H5B	−0.0278	0.0706	0.0658	0.071*
C6	0.2655 (7)	0.04127 (16)	0.2037 (4)	0.0884 (11)
H6A	0.3816	0.0643	0.2737	0.106*
H6B	0.3800	0.0234	0.1317	0.106*
C7	0.1225 (9)	−0.01936 (19)	0.2712 (5)	0.1121 (15)
H7A	0.0049	−0.0019	0.3409	0.168*
H7B	0.2545	−0.0502	0.3143	0.168*
H7C	0.0173	−0.0444	0.2012	0.168*
C8	0.2658 (5)	0.33973 (12)	0.0891 (3)	0.0549 (7)
H8A	0.4412	0.3597	0.1098	0.082*
H8B	0.1528	0.3462	0.1677	0.082*
H8C	0.1842	0.3624	0.0085	0.082*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0502 (11)	0.0624 (12)	0.0563 (11)	−0.0052 (8)	0.0315 (9)	−0.0021 (9)
O2	0.0663 (13)	0.0528 (12)	0.0744 (13)	−0.0101 (9)	0.0330 (10)	0.0005 (9)
N1	0.0359 (10)	0.0442 (11)	0.0423 (11)	0.0006 (8)	0.0138 (9)	−0.0002 (8)
N2	0.0406 (11)	0.0489 (12)	0.0462 (12)	−0.0010 (9)	0.0193 (9)	0.0035 (9)

C1	0.0354 (13)	0.0546 (16)	0.0409 (13)	0.0004 (11)	0.0102 (10)	0.0029 (11)
C2	0.0328 (12)	0.0492 (14)	0.0370 (12)	0.0008 (10)	0.0124 (10)	−0.0005 (10)
C3	0.0421 (14)	0.0479 (15)	0.0485 (14)	0.0058 (10)	0.0176 (11)	−0.0010 (11)
C4	0.0403 (13)	0.0466 (14)	0.0498 (15)	0.0019 (10)	0.0158 (11)	0.0032 (11)
C5	0.0573 (17)	0.0537 (16)	0.0690 (18)	−0.0030 (12)	0.0266 (14)	0.0048 (13)
C6	0.081 (2)	0.063 (2)	0.122 (3)	−0.0029 (17)	0.015 (2)	0.0266 (19)
C7	0.121 (3)	0.070 (2)	0.147 (4)	−0.003 (2)	0.024 (3)	0.045 (2)
C8	0.0584 (17)	0.0454 (15)	0.0622 (17)	−0.0001 (12)	0.0198 (13)	−0.0057 (12)

Geometric parameters (Å, °)

O1—C1	1.317 (3)	C5—C6	1.468 (4)
O1—H1	0.84 (3)	C5—H5A	0.9700
O2—C1	1.195 (3)	C5—H5B	0.9700
N1—N2	1.346 (2)	C6—C7	1.514 (4)
N1—C2	1.352 (3)	C6—H6A	0.9700
N1—C8	1.443 (3)	C6—H6B	0.9700
N2—C4	1.328 (3)	C7—H7A	0.9600
C1—C2	1.475 (3)	C7—H7B	0.9600
C2—C3	1.365 (3)	C7—H7C	0.9600
C3—C4	1.396 (3)	C8—H8A	0.9600
C3—H3	0.9300	C8—H8B	0.9600
C4—C5	1.488 (3)	C8—H8C	0.9600
C1—O1—H1	110 (2)	C4—C5—H5B	108.6
N2—N1—C2	110.26 (19)	H5A—C5—H5B	107.6
N2—N1—C8	119.39 (17)	C5—C6—C7	112.9 (3)
C2—N1—C8	130.34 (19)	C5—C6—H6A	109.0
C4—N2—N1	107.06 (17)	C7—C6—H6A	109.0
O2—C1—O1	124.6 (2)	C5—C6—H6B	109.0
O2—C1—C2	124.5 (2)	C7—C6—H6B	109.0
O1—C1—C2	111.0 (2)	H6A—C6—H6B	107.8
N1—C2—C3	107.28 (18)	C6—C7—H7A	109.5
N1—C2—C1	122.6 (2)	C6—C7—H7B	109.5
C3—C2—C1	130.2 (2)	H7A—C7—H7B	109.5
C2—C3—C4	105.9 (2)	C6—C7—H7C	109.5
C2—C3—H3	127.0	H7A—C7—H7C	109.5
C4—C3—H3	127.0	H7B—C7—H7C	109.5
N2—C4—C3	109.5 (2)	N1—C8—H8A	109.5
N2—C4—C5	120.9 (2)	N1—C8—H8B	109.5
C3—C4—C5	129.6 (2)	H8A—C8—H8B	109.5
C6—C5—C4	114.5 (2)	N1—C8—H8C	109.5
C6—C5—H5A	108.6	H8A—C8—H8C	109.5
C4—C5—H5A	108.6	H8B—C8—H8C	109.5
C6—C5—H5B	108.6		
C2—N1—N2—C4	0.0 (2)	N1—C2—C3—C4	−0.2 (3)
C8—N1—N2—C4	−179.6 (2)	C1—C2—C3—C4	178.4 (2)
N2—N1—C2—C3	0.2 (2)	N1—N2—C4—C3	−0.1 (3)
C8—N1—C2—C3	179.7 (2)	N1—N2—C4—C5	179.8 (2)
N2—N1—C2—C1	−178.6 (2)	C2—C3—C4—N2	0.2 (3)

C8—N1—C2—C1	1.0 (4)	C2—C3—C4—C5	−179.6 (3)
O2—C1—C2—N1	4.9 (4)	N2—C4—C5—C6	−123.6 (3)
O1—C1—C2—N1	−175.1 (2)	C3—C4—C5—C6	56.3 (4)
O2—C1—C2—C3	−173.5 (3)	C4—C5—C6—C7	174.6 (3)
O1—C1—C2—C3	6.4 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2^{i}	0.84 (3)	1.88 (3)	2.712 (3)	169 (3)
C5—H5A···O2^{ii}	0.97	2.48	3.430 (4)	166

Symmetry codes: (i) *x*+1, −*y*+1/2, *z*−1/2; (ii) *x*−1, −*y*+1/2, *z*+1/2.

Fig. 1

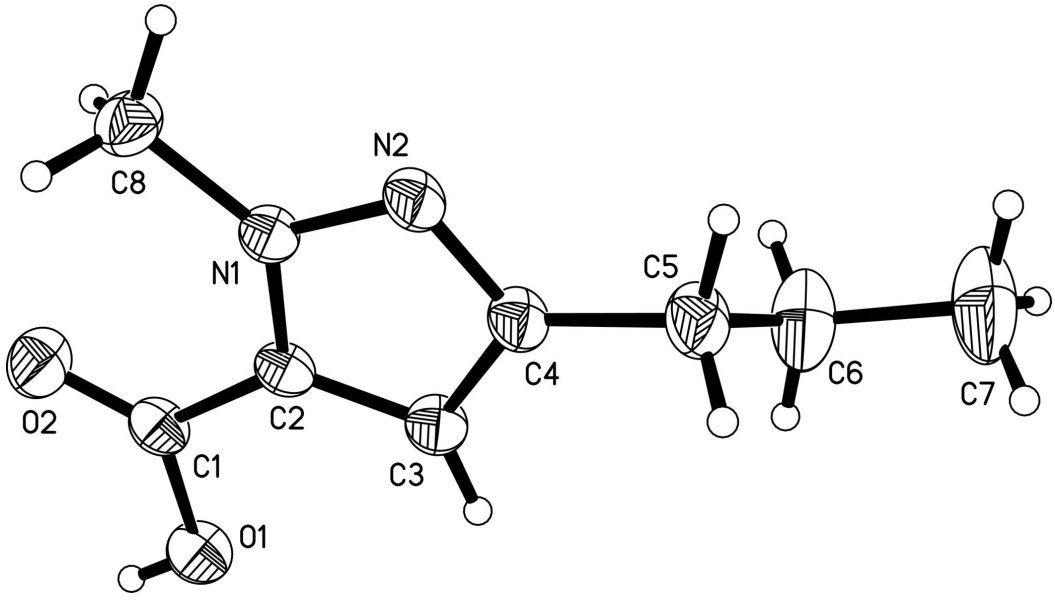

Fig. 2