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Key indicators

Single-crystal X-ray study
 $T = 183\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.052
 wR factor = 0.142
Data-to-parameter ratio = 12.5

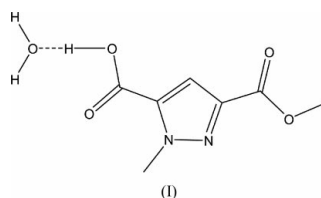
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Methyl 5-carboxyl-1-methylpyrazole-3-carboxylate monohydrate

The crystal structure of the title compound, $\text{C}_7\text{H}_8\text{N}_2\text{O}_4 \cdot \text{H}_2\text{O}$, has been determined in the monoclinic system with the space group $C2/c$. It is an intermediate compound for synthesizing oligomeric carboxamides, which can bind to DNA by lodging in the minor groove. The molecules are linked into two-dimensional sheets by $\text{O}-\text{H} \cdots \text{N}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen-bonding interactions. The sheets form a three-dimensional network *via* weak intermolecular $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds.

Comment

The title compound, (I), is a key intermediate used to synthesize oligomeric carboxamides, which can bind to DNA by lodging in the minor groove (Lee *et al.*, 1989). Although (I) was synthesized in 1989 (Lee *et al.*, 1989), its crystal structure has not been reported up to now.



There is a methoxycarbonyl group on atom C2 and a carboxyl group on atom C4 of the title molecule. The existence of one carboxyl group and one pyrazole N atom allows the molecule to function as both an H-atom acceptor and a donor. The shape of the molecule enables the compound to form various $\text{O}-\text{H} \cdots \text{N}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. It is well known that hydrogen bonds play a significant role in the construction of supramolecular organic systems because their strength contributes to crystallization (Desiraju, 1995). In this crystal structure, the molecules of the title compound are linked into two-dimensional sheets *via* different intermolecular hydrogen bonds, specifically between atoms O5 and H5B and the pyrazole ring atom N2; between atoms O5 and

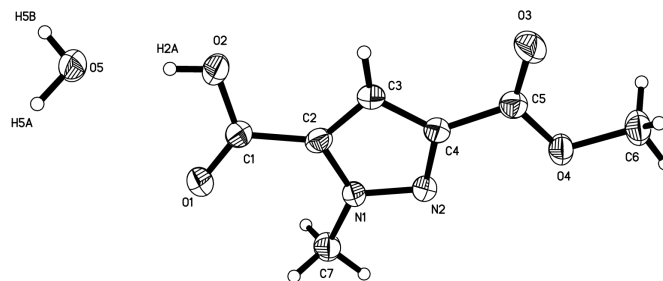


Figure 1

A view of the molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as small spheres of arbitrary radii.

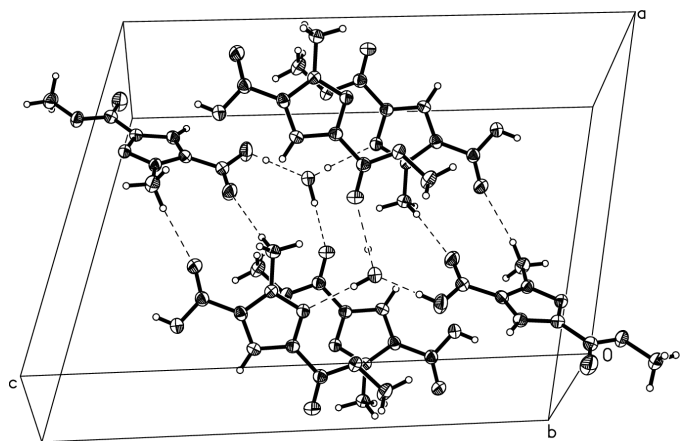


Figure 2

A packing diagram of (I). Hydrogen bonds are indicated by dashed lines.

H5A and the ester carbonyl atom O3; and between atoms O2 and H2A and the water atom O5 (Figs. 1 and 2, and Table 2). More interestingly, we detect weak intermolecular C—H...O hydrogen bonds (Desiraju, 1996; Steiner, 1997) between the methyl H atoms on atom C7 and the carbonyl atoms O1 and O3 (Table 2). These interactions play an important role in forming the three-dimensional network in the crystal structure.

The geometric parameters of (I) are listed in Table 1. The molecular configuration and crystal packing are illustrated in Figs. 1 and 2. Inspection of these values indicates that there is delocalization of the π -electron density in the pyrazole ring. The asymmetric unit of the title compound contains a water molecule, and there are some similarities between the geometries (bond lengths and angles) of (I) and of 3,5-pyrazoledicarboxylic acid (Ching *et al.*, 2000). However, as there is a methyl group at the N1 position, the N1—C2—C1 angle [123.2 (2)°] is larger than the N2=C4—C5 angle [120.8 (2)°]. The dihedral angle between the O3=C5—O4 ester plane and the pyrazole plane is 2.6 (3)°, and the dihedral angle between the O1=C1—O2 carboxyl-group plane and the pyrazole plane is 14.3 (1)°.

Experimental

Compound (I) was synthesized according to the method described by Lee *et al.* (1989). ¹H NMR (CDCl₃): δ 3.96 (s, 3H, NCH₃), 4.28 (s, 3H, COOCH₃), 7.45 (s, 1H, CH). M.p. 403 K. The compound (100 mg) was dissolved in dilute hydrochloric acid (10 ml). This solution was allowed to evaporate slowly at room temperature over a period of one month, yielding colorless crystals of the compound suitable for X-ray analysis.

Crystal data

C₇H₈N₂O₄·H₂O
M_r = 202.17
 Monoclinic, C2/c
a = 13.641 (3) Å
b = 7.3197 (15) Å
c = 18.660 (4) Å
 β = 104.62 (3)°
V = 1802.8 (6) Å³
Z = 8

D_x = 1.490 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 4940 reflections
 θ = 2.3–26.6°
 μ = 0.13 mm⁻¹
T = 183 (2) K
 Block, colorless
 0.30 × 0.30 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.963, *T*_{max} = 0.975
 3564 measured reflections

1590 independent reflections
 1337 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.023
 θ _{max} = 25.0°
h = -12 → 16
k = -8 → 7
l = -22 → 22

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.052
wR(*F*²) = 0.142
S = 1.08
 1590 reflections
 127 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.078P)^2 + 0.9903P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.39 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.30 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

N1—N2	1.337 (3)	C2—C3	1.375 (3)
N1—C2	1.361 (3)	C3—C4	1.393 (3)
N1—C7	1.460 (3)	C4—C5	1.472 (3)
N2—C4	1.343 (3)	O3—C5	1.203 (3)
O1—C1	1.201 (3)	O4—C5	1.327 (3)
O2—C1	1.311 (3)	O4—C6	1.449 (3)
C1—C2	1.476 (3)		
N2—N1—C2	111.88 (18)	N1—C2—C1	123.2 (2)
N2—N1—C7	118.15 (18)	C3—C2—C1	129.9 (2)
C2—N1—C7	129.77 (19)	C2—C3—C4	104.9 (2)
N1—N2—C4	105.05 (18)	N2—C4—C3	111.3 (2)
C5—O4—C6	116.98 (19)	N2—C4—C5	120.8 (2)
O1—C1—O2	124.2 (2)	C3—C4—C5	127.8 (2)
O1—C1—C2	123.9 (2)	O3—C5—O4	124.5 (2)
O2—C1—C2	111.8 (2)	O3—C5—C4	123.4 (2)
N1—C2—C3	106.86 (19)	O4—C5—C4	112.1 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H5B...N2 ⁱ	0.84	2.01	2.856 (2)	176
O5—H5A...O3 ⁱⁱ	0.95	1.91	2.854 (2)	173
C7—H7A...O3 ⁱⁱⁱ	0.98	2.58	3.489 (3)	154
C7—H7C...O1 ^{iv}	0.98	2.38	3.332 (3)	163
O2—H2A...O5	0.84	1.71	2.544 (2)	177

Symmetry codes: (i) $x, -y, \frac{1}{2} + z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iv) $2 - x, y, \frac{3}{2} - z$.

All H atoms, except the water H atoms, were placed at calculated positions, while the locations of water atoms H5A and H5B were obtained from a difference map. All H atoms were treated as riding, with *U*_{iso}(H) values constrained to be 1.2*U*_{eq} of the carrier atoms (1.5*U*_{eq} for the CH₃ group).

Data collection: SMART (Siemens, 1996); cell refinement: SMART; data reduction: SAINT (Siemens, 1996) and SHELXTL (Siemens, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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