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#### Key indicators

Single-crystal X-ray study  
 $T = 100\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$   
 $R$  factor = 0.046  
 $wR$  factor = 0.115  
Data-to-parameter ratio = 15.3

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

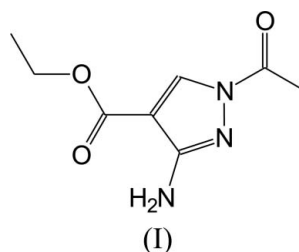
## Ethyl 1-acetyl-3-amino-1*H*-pyrazole-4-carboxylate, a tetragonal structure with $Z' = 4$

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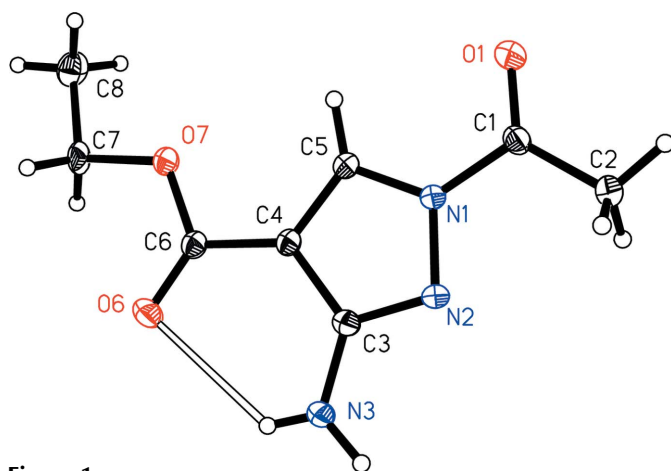
The title compound,  $\text{C}_8\text{H}_{11}\text{N}_3\text{O}_3$ , crystallizes with  $Z' = 4$ . One pyrazole N atom is substituted and excluded from intermolecular contacts. The amine N, acetyl O and an ester O atom are involved in the formation of nearly planar molecular layers. The layers are perpendicular to the  $c$  axis, with an interlayer distance of 3.333 Å. The hydrogen-bonding patterns are similar for each molecule, *i.e.* intramolecular  $\text{N}-\text{H}\cdots\text{O}$ , as well as intermolecular  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}-\text{H}\cdots\text{N}(\text{pyrazole})$ , bonds are present.

#### Comment

For crystal engineering, the most interesting cases of molecular association are those with cyclic patterns linking high numbers of molecules. Some mono-, di- and tri-substituted NH-pyrazole derivatives crystallize forming cyclic patterns of  $-\text{N1}-\text{H}\cdots\text{N2}-\text{N1}-\text{H}\cdots\text{N2}-$  hydrogen bonds between pyrazole rings [Cambridge Structural Database (CSD), Version 5.27; Allen, 2002]. Depending on the type, size and position of substituents, the primary motifs (Etter *et al.*, 1990) are  $R_2^2(6)$  dimers,  $R_3^3(9)$  trimers,  $R_4^4(12)$  tetramers or even  $R_6^6(18)$  hexamers (Haghiri *et al.*, 2002; CSD refcode HUMLUW). The CSD refcodes for selected crystal structures with dimeric clusters are: ALACEV, ATOWAH, CAMFUS, CIOHIT, FIWTIP, GISZIR, HEHTUJ, IXAQUT, LADBEX, MAFWAS, OBIZAA, VEHCOA, WILBAU, WILBEY, YEYQOI and YULNUO; with trimeric clusters: FITQAA, RIKNOO, DASXEA, HEHVAR, LETCES, PAMTAY, WIKZUL, LABHEB, TIWKIT, UHENUQ, VILPEL, GOQXIT and HOQHUUQ; and with tetrameric clusters: QAMQEA, QOFWUD, MEPHPY, PAHKIT, QOFWOX, RUPSAW, SAKQAX, HUMLUW01, DIRKOE, ESUJOR and QOFXAK. In these crystal structures, the molecular clusters adopt crystallographic symmetry (*e.g.*  $\bar{1}$ ,  $\bar{3}$  and  $\bar{4}$ ), or they are built of symmetry-independent molecules ( $Z'$  in the range 2–6).

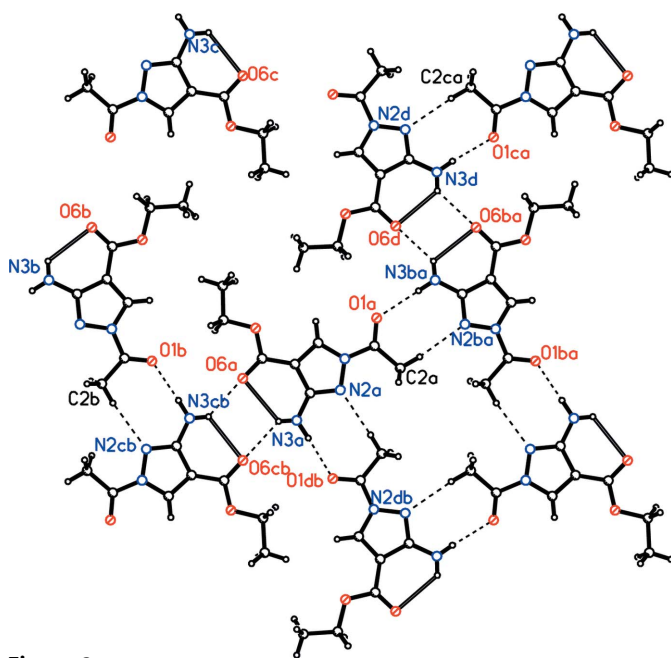


A search of the CSD for crystal structures of N1-substituted pyrazole (with simple substituents) containing two or more symmetry-independent molecules revealed only a few exam-



**Figure 1**

The structure of one of the four independent molecules of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The open line indicates the intramolecular N—H···O hydrogen bond.

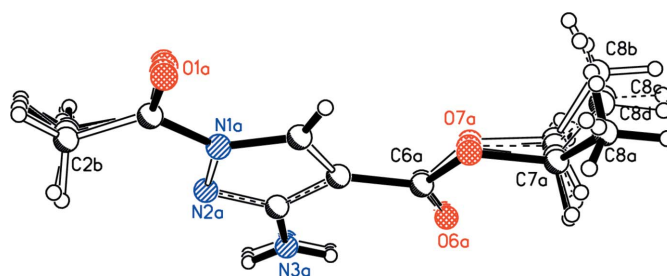


**Figure 2**

Part of the crystal structure of (I), showing the layer formed via intermolecular N—H···O and C—H···N hydrogen bonds (dashed lines).

ples (e.g. refcodes BOLQEY, INEPIA, RBZICB and TEQZAQ). Analysis of the intermolecular contacts shows that only C—H···N/O/π interactions and stacking are present. We have now synthesized the new title N1-pyrazole derivative, 1-acetyl-3-amino-4-carboxy-1*H*-pyrazole, (I), the molecules of which are able to form stronger hydrogen bonds of the N—H···O type, and present its structure here.

The asymmetric unit of the tetragonal crystal structure of (I) contains four independent molecules, (IA)–(ID), which can be considered as rotated about a pseudo-fourfold axis (located between methyl groups; Fig. 1). The crystal structure is built of molecular layers, perpendicular to the [001] direction, the separation distance being 3.333 Å, *i.e.*  $\frac{1}{4}$  of the *c* parameter. All molecules are nearly planar; their bond lengths are equal to



**Figure 3**

A fit of the pyrazole rings of the four symmetry-independent molecules of (I). The distance between atoms C8A and C8B is 1.227 Å. The C6—O7—C7—C8 torsion angles are  $-169.9$  (1) and  $166.2$  (3) $^\circ$  for (IA) and (IB), respectively.

within  $2\sigma$  (Table 1) and they have similar patterns of intra- and intermolecular N—H···O and C—H···N hydrogen bonds (Fig. 2 and Table 2). The donor···acceptor distances of the weak C—H···N bonds range from 3.406 (2) to 3.475 (2) Å.

Molecules (IA)–(ID) adopt slightly different conformations of the terminal methyl and ethyl groups (Fig. 3). The transformation of the molecular layers by the  $4_3$  screw-axis causes a different environment for each symmetry-independent molecule (Fig. 4). To date, only four crystal structures with the space group  $P4_1$  or  $P4_3$  and  $Z' = 4$  have been reported (CSD refcodes BEXTTE, CPSCOA, ZEPKUA and XOQQOJ).

## Experimental

Acetic anhydride (7.5 mmol) was added to a suspension of 3-amino-4-carboxy-2*H*-pyrazole (5 mmol) and dimethylaminopyridine (1 mmol), and after 1 h the white crystalline precipitate which formed was filtered off and washed with dimethylformamide to give (I). Single crystals for X-ray analysis were obtained by recrystallization from methanol.

### Crystal data

$C_8H_{11}N_3O_3$   
 $M_r = 197.20$   
 Tetragonal,  $P4_3$   
 $a = 16.887$  (6) Å  
 $c = 13.332$  (5) Å  
 $V = 3802$  (2) Å<sup>3</sup>  
 $Z = 16$

$D_x = 1.378$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 Prism, colourless  
 $0.63 \times 0.52 \times 0.35$  mm

### Data collection

Kuma KM4 CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2001)  
 $T_{\min} = 0.929$ ,  $T_{\max} = 0.963$

37699 measured reflections  
 7874 independent reflections  
 6125 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.034$   
 $\theta_{\max} = 37.5^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.115$   
 $S = 1.03$   
 7874 reflections  
 513 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.071P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.48$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.36$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

N1A—C5A	1.353 (2)	N1C—C5C	1.361 (2)
N1A—N2A	1.391 (2)	N1C—N2C	1.392 (2)
N2A—C3A	1.333 (2)	N2C—C3C	1.332 (2)
C3A—C4A	1.441 (2)	C3C—C4C	1.440 (2)
C4A—C5A	1.377 (2)	C4C—C5C	1.373 (2)
N1B—C5B	1.363 (2)	N1D—C5D	1.356 (2)
N1B—N2B	1.390 (2)	N1D—N2D	1.394 (2)
N2B—C3B	1.335 (2)	N2D—C3D	1.333 (2)
C3B—C4B	1.446 (2)	C3D—C4D	1.442 (2)
C4B—C5B	1.365 (2)	C4D—C5D	1.369 (2)

**Table 2**

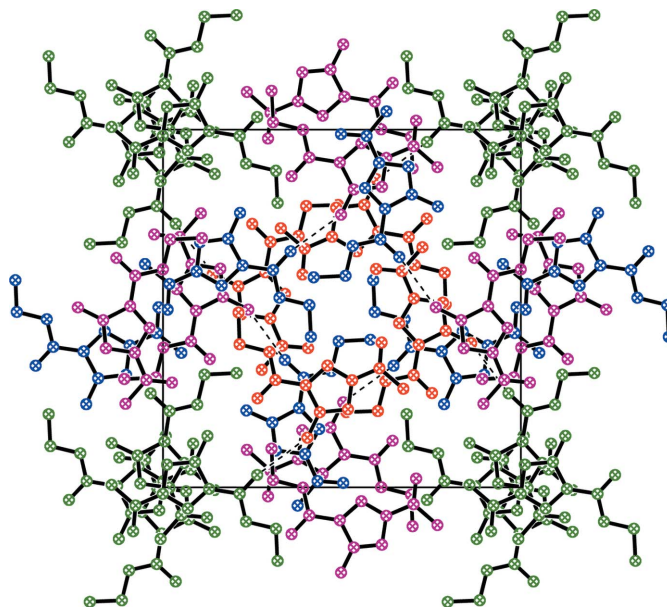
Hydrogen-bond geometry (Å, °).

<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>
N3A—H3A2...O6A	0.88	2.43	3.003 (2)	124
N3A—H3A2...O6C <sup>i</sup>	0.88	2.26	2.948 (2)	135
N3A—H3A1...O1D <sup>i</sup>	0.88	2.14	3.015 (2)	173
N3B—H3B2...O6B	0.88	2.40	2.977 (2)	124
N3B—H3B2...O6D <sup>ii</sup>	0.88	2.25	2.941 (2)	136
N3B—H3B1...O1A <sup>ii</sup>	0.88	2.18	3.050 (2)	171
N3C—H3C2...O6C	0.88	2.41	2.984 (2)	123
N3C—H3C2...O6A <sup>iii</sup>	0.88	2.27	2.964 (2)	135
N3C—H3C1...O1B <sup>iii</sup>	0.88	2.15	3.025 (2)	175
N3D—H3D2...O6D	0.88	2.43	3.006 (2)	123
N3D—H3D1...O1C <sup>iv</sup>	0.88	2.09	2.966 (2)	175
N3D—H3D2...O6B <sup>iv</sup>	0.88	2.26	2.979 (2)	139

Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $x, y - 1, z$ ; (iii)  $x - 1, y, z$ ; (iv)  $x, y + 1, z$ .

Of the two possible enantiomeric space groups,  $P4_1$  or  $P4_3$ , the latter was used arbitrarily for the final refinement; in the absence of significant anomalous scattering, the correct space group is unknown. Friedel pairs were merged. All H atoms were positioned geometrically and allowed to ride on their parent atom, with C—H bond lengths of 0.95 Å for pyrazole H5 atoms, 0.99 Å for methylene H atoms and 0.98 Å for methyl H atoms, and with N—H distances of 0.88 Å.  $U_{\text{iso}}(\text{H})$  values were set equal to  $1.5U_{\text{eq}}(\text{C})$  for methyl groups and  $1.2U_{\text{eq}}(\text{C}, \text{N})$  for the remaining atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2001); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*



**Figure 4**

The crystal packing of (I), viewed down the *c* axis. Molecules (IA) are red, (IB) purple, (IC) green and (ID) blue. H atoms have been omitted.

(Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97* and *enCIFer* (Allen *et al.*, 2004).

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