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Ethyl 5-amino-1-(6-chloropyridazin-3-yl)-1*H*-pyrazole-4-carboxylate

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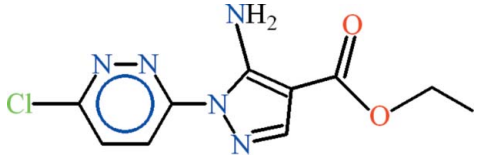
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.101; data-to-parameter ratio = 13.0.

In the title compound, $C_{10}H_{10}ClN_5O_2$, the dihedral angle between the aromatic rings is 0.16 (9)°. Two S(6) ring motifs are formed due to intramolecular N—H···N and N—H···O hydrogen bonds. In the crystal, inversion dimers linked by pairs of N—H···N hydrogen bonds generate $R_2^2(14)$ [or $R_4^4(10)$ *via* the intramolecular hydrogen bonds] ring motifs. Polymeric chains propagating in [210] are formed as a result of interlinking the dimers by pairs of C—H···N interactions, completing $R_2^2(6)$ ring motifs.

Related literature

For biochemical background and related structures, see: Ather *et al.* (2010*a*,*b*,*c*). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{10}H_{10}ClN_5O_2$
M_r = 267.68
Triclinic, $P\overline{1}$
a = 5.3618 (3) Å
b = 8.6168 (4) Å
c = 13.1585 (7) Å
α = 77.734 (2)°
β = 82.928 (1)°
γ = 86.722 (2)°
V = 589.24 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 296 K
0.25 × 0.20 × 0.08 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.982, T_{max} = 0.988
8832 measured reflections
2125 independent reflections
1721 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.101
S = 1.06
2125 reflections
164 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···N1	0.86	2.17	2.775 (2)	127
N5—H5B···O2	0.86	2.40	2.942 (2)	122
N5—H5B···N2^{i}	0.86	2.41	3.017 (2)	128
C5—H5···N4^{ii}	0.93	2.53	3.313 (2)	142

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5619).

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Acta Cryst. (2010). E**66**, o2445 [https://doi.org/10.1107/S1600536810034240]

Ethyl 5-amino-1-(6-chloropyridazin-3-yl)-1*H*-pyrazole-4-carboxylate

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S1. Comment

In continuation of our studies of pyrazolylpyridazine derivatives (Ather *et al.*, 2010*a, b, c*), the title compound (I, Fig. 1) is being reported here.

In (I), the 1-(6-chloropyridazin-3-yl)-1*H*-pyrazol-5-amine moiety A (C1—C7/N1—N5/CL1) and ethyl formate group B (C8—C10/O1/O2) are planar with r. m. s. deviations of 0.0026 and 0.0293 Å, respectively. The dihedral angle between A/B is 3.09 (12)°. There exist two S(6) ring motifs (Bernstein *et al.*, 1995) due to N–H···N and N—H···O types of intramolecular H-bondings (Table 1, Fig. 1). The molecules are dimerized due to N–H···N type of H-bonding (Table 2, Fig. 2) with $R_4^4(10)$ ring motifs. The dimers are interliked in the from of polymeric chains due to H-bondings of C—H···N type with $R_2^2(6)$ ring motifs (Table 2, Fig. 2).

S2. Experimental

3-Chloro-6-hydrazinylpyridazine (2 g, 13.84 mmol) and ethylethoxymethylene cyanoacetate (2.35 g, 13.84 mmol) were dissolved in acetic acid (10 ml). The obtained reaction mixture was refluxed for 4 h and cooled to room temperature. The resulting product was poured in 100 ml of distiled water and the precipitates were formed. The precipitates obtained by filteration were washed three times by water. The crude material obtained was dried and purified by column chromatography. The final product was re-crystallized in benzene to obtain light brown plates of (I).

S3. Refinement

The H-atoms were positioned geometrically (N–H = 0.86, C–H = 0.93–0.97 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) = xU_{eq}(C, N), where x = 1.5 for methyl and x = 1.2 for all other H-atoms.

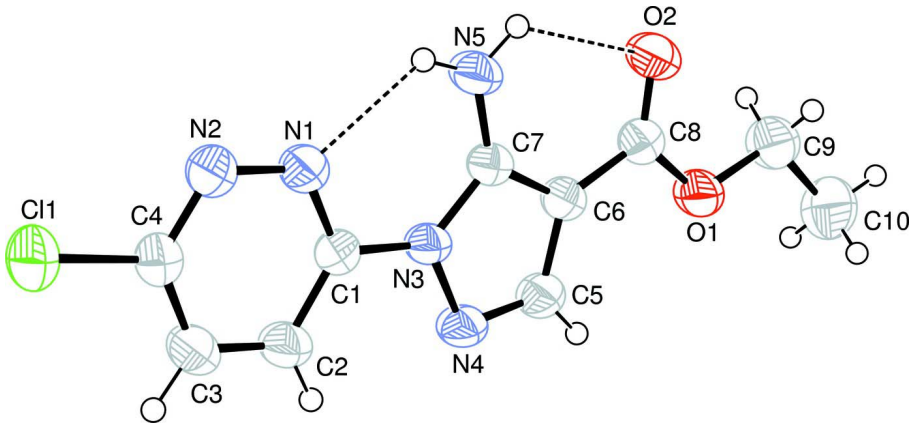

Figure 1

View of (I) with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown as small spheres of arbitrary radius. The dotted lines indicate the intramolecular H-bonds.

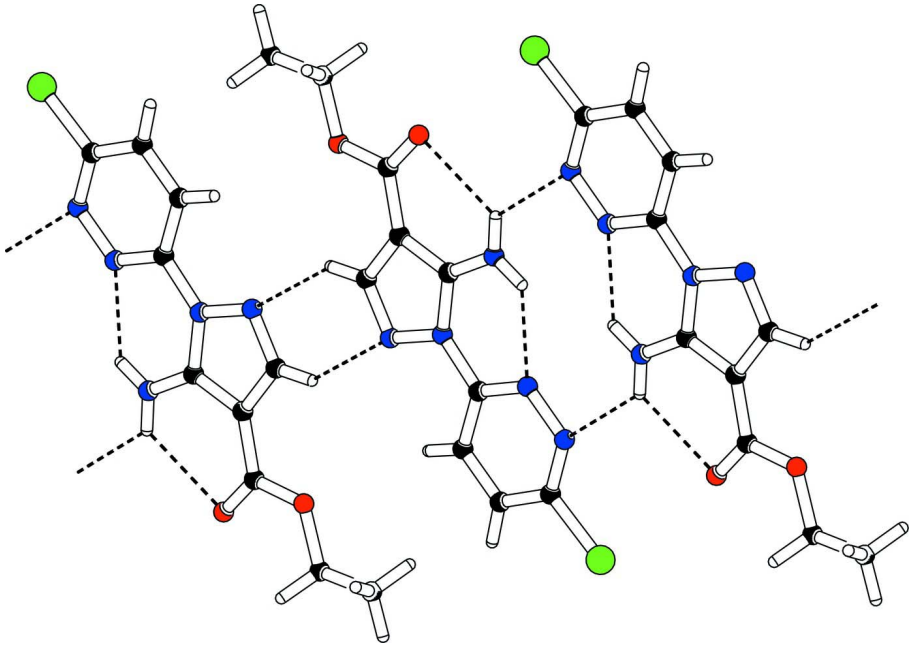

Figure 2

Packing diagram of (I) showing that the molecules form dimers, which are interlinked in the form of polymeric chains.

Ethyl 5-amino-1-(6-chloropyridazin-3-yl)-1*H*-pyrazole-4-carboxylate

Crystal data

$C_{10}H_{10}ClN_5O_2$
$M_r = 267.68$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 5.3618\ (3)$ Å
$b = 8.6168\ (4)$ Å
$c = 13.1585\ (7)$ Å
$\alpha = 77.734\ (2)°$
$\beta = 82.928\ (1)°$
$\gamma = 86.722\ (2)°$
$V = 589.24\ (5)$ Å^3
$Z = 2$
$F(000) = 276$
$D_x = 1.509$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1721 reflections
$\theta = 2.4–25.2°$
$\mu = 0.33$ mm^{-1}

T = 296 K
Plate, light brown

0.25 × 0.20 × 0.08 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.10 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.982, T_{max} = 0.988

8832 measured reflections
2125 independent reflections
1721 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 25.2°, θ_{min} = 2.4°
h = −6→6
k = −10→10
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.101
S = 1.06
2125 reflections
164 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.1261P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Special details

Geometry. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Cl1	1.21255 (10)	0.81971 (7)	−0.39777 (4)	0.0677 (2)
O1	0.0151 (3)	0.69934 (15)	0.27701 (10)	0.0604 (4)
O2	0.3413 (3)	0.52161 (16)	0.27988 (10)	0.0640 (5)
N1	0.8615 (3)	0.69752 (18)	−0.12132 (12)	0.0510 (5)
N2	1.0286 (3)	0.70752 (18)	−0.20741 (12)	0.0542 (5)
N3	0.4983 (2)	0.78156 (16)	−0.03130 (10)	0.0431 (5)
N4	0.2872 (3)	0.88448 (17)	−0.03037 (12)	0.0502 (5)
N5	0.6846 (3)	0.56546 (17)	0.08430 (12)	0.0555 (5)
C1	0.6639 (3)	0.79680 (19)	−0.12305 (13)	0.0415 (5)
C2	0.6174 (3)	0.9141 (2)	−0.21063 (15)	0.0533 (6)
C3	0.7854 (3)	0.9223 (2)	−0.29680 (15)	0.0561 (6)
C4	0.9885 (3)	0.8155 (2)	−0.29040 (14)	0.0481 (6)
C5	0.1714 (3)	0.8415 (2)	0.06357 (14)	0.0500 (6)
C6	0.2931 (3)	0.7149 (2)	0.12671 (13)	0.0445 (5)

C7	0.5052 (3)	0.67718 (19)	0.06360 (13)	0.0422 (5)
C8	0.2250 (3)	0.6341 (2)	0.23350 (14)	0.0486 (6)
C9	−0.0707 (5)	0.6236 (3)	0.38284 (17)	0.0732 (8)
C10	−0.2913 (4)	0.7155 (3)	0.42191 (19)	0.0806 (9)
H2	0.47768	0.98310	−0.20953	0.0639*
H3	0.76539	0.99675	−0.35797	0.0673*
H5	0.02210	0.89012	0.08673	0.0600*
H5A	0.80622	0.55512	0.03686	0.0665*
H5B	0.67887	0.50366	0.14512	0.0665*
H9A	0.06306	0.61935	0.42685	0.0879*
H9B	−0.11731	0.51568	0.38514	0.0879*
H10A	−0.42248	0.71987	0.37778	0.1208*
H10B	−0.24295	0.82139	0.42099	0.1208*
H10C	−0.35108	0.66460	0.49222	0.1208*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0694 (3)	0.0765 (4)	0.0499 (3)	0.0052 (3)	0.0126 (2)	−0.0098 (3)
O1	0.0675 (8)	0.0591 (8)	0.0434 (7)	0.0132 (6)	0.0109 (6)	0.0005 (6)
O2	0.0691 (9)	0.0651 (9)	0.0483 (8)	0.0172 (7)	−0.0037 (7)	0.0029 (6)
N1	0.0510 (8)	0.0536 (9)	0.0424 (8)	0.0121 (7)	0.0004 (7)	−0.0037 (7)
N2	0.0530 (9)	0.0583 (10)	0.0457 (9)	0.0122 (7)	0.0024 (7)	−0.0064 (8)
N3	0.0442 (8)	0.0407 (8)	0.0398 (8)	0.0096 (6)	−0.0023 (6)	−0.0027 (6)
N4	0.0469 (8)	0.0485 (8)	0.0486 (9)	0.0168 (7)	−0.0014 (7)	−0.0022 (7)
N5	0.0544 (9)	0.0579 (10)	0.0445 (9)	0.0196 (7)	−0.0021 (7)	0.0032 (7)
C1	0.0422 (9)	0.0420 (9)	0.0395 (9)	0.0041 (7)	−0.0040 (7)	−0.0085 (7)
C2	0.0535 (10)	0.0515 (10)	0.0480 (11)	0.0137 (8)	−0.0039 (8)	−0.0003 (8)
C3	0.0608 (11)	0.0570 (11)	0.0428 (10)	0.0081 (9)	−0.0026 (9)	0.0026 (9)
C4	0.0512 (10)	0.0512 (10)	0.0403 (10)	0.0011 (8)	−0.0008 (8)	−0.0093 (8)
C5	0.0472 (9)	0.0500 (10)	0.0479 (10)	0.0106 (8)	0.0013 (8)	−0.0064 (8)
C6	0.0462 (9)	0.0451 (9)	0.0390 (9)	0.0058 (7)	−0.0027 (7)	−0.0050 (8)
C7	0.0441 (9)	0.0404 (9)	0.0400 (9)	0.0047 (7)	−0.0058 (7)	−0.0050 (7)
C8	0.0526 (10)	0.0482 (10)	0.0429 (10)	0.0042 (8)	−0.0034 (8)	−0.0073 (8)
C9	0.0894 (15)	0.0670 (13)	0.0492 (12)	0.0089 (11)	0.0189 (11)	0.0010 (10)
C10	0.0777 (15)	0.0906 (17)	0.0658 (15)	0.0008 (13)	0.0197 (12)	−0.0161 (13)

Geometric parameters (Å, º)

Cl1—C4	1.7337 (18)	C2—C3	1.351 (3)
O1—C8	1.348 (2)	C3—C4	1.384 (2)
O1—C9	1.438 (3)	C5—C6	1.405 (2)
O2—C8	1.214 (2)	C6—C7	1.389 (2)
N1—N2	1.346 (2)	C6—C8	1.442 (2)
N1—C1	1.323 (2)	C9—C10	1.486 (4)
N2—C4	1.307 (2)	C2—H2	0.9300
N3—N4	1.398 (2)	C3—H3	0.9300
N3—C1	1.395 (2)	C5—H5	0.9300

N3—C7	1.378 (2)	C9—H9A	0.9700
N4—C5	1.301 (2)	C9—H9B	0.9700
N5—C7	1.332 (2)	C10—H10A	0.9600
N5—H5A	0.8600	C10—H10B	0.9600
N5—H5B	0.8600	C10—H10C	0.9600
C1—C2	1.400 (2)		

C8—O1—C9	115.59 (16)	N3—C7—N5	124.20 (15)
N2—N1—C1	119.35 (15)	N3—C7—C6	105.71 (14)
N1—N2—C4	118.42 (16)	O1—C8—O2	123.39 (16)
N4—N3—C1	118.30 (13)	O1—C8—C6	111.74 (15)
N4—N3—C7	111.47 (12)	O2—C8—C6	124.87 (16)
C1—N3—C7	130.23 (13)	O1—C9—C10	109.1 (2)
N3—N4—C5	104.02 (14)	C1—C2—H2	122.00
H5A—N5—H5B	120.00	C3—C2—H2	122.00
C7—N5—H5A	120.00	C2—C3—H3	121.00
C7—N5—H5B	120.00	C4—C3—H3	121.00
N1—C1—N3	116.76 (15)	N4—C5—H5	123.00
N1—C1—C2	123.38 (16)	C6—C5—H5	123.00
N3—C1—C2	119.86 (15)	O1—C9—H9A	110.00
C1—C2—C3	116.75 (16)	O1—C9—H9B	110.00
C2—C3—C4	117.32 (17)	C10—C9—H9A	110.00
N2—C4—C3	124.78 (17)	C10—C9—H9B	110.00
Cl1—C4—C3	119.87 (14)	H9A—C9—H9B	108.00
Cl1—C4—N2	115.35 (13)	C9—C10—H10A	109.00
N4—C5—C6	113.70 (15)	C9—C10—H10B	109.00
C5—C6—C7	105.11 (15)	C9—C10—H10C	109.00
C5—C6—C8	130.39 (16)	H10A—C10—H10B	109.00
C7—C6—C8	124.51 (15)	H10A—C10—H10C	109.00
N5—C7—C6	130.09 (16)	H10B—C10—H10C	109.00

C9—O1—C8—O2	−2.0 (3)	C1—N3—C7—C6	−179.82 (16)
C9—O1—C8—C6	178.45 (17)	N3—N4—C5—C6	0.2 (2)
C8—O1—C9—C10	176.03 (17)	N1—C1—C2—C3	0.6 (3)
C1—N1—N2—C4	−0.3 (2)	N3—C1—C2—C3	179.95 (16)
N2—N1—C1—N3	−179.52 (15)	C1—C2—C3—C4	−0.6 (2)
N2—N1—C1—C2	−0.1 (3)	C2—C3—C4—Cl1	−179.69 (14)
N1—N2—C4—Cl1	−179.85 (13)	C2—C3—C4—N2	0.2 (3)
N1—N2—C4—C3	0.2 (3)	N4—C5—C6—C7	−0.2 (2)
C1—N3—N4—C5	179.72 (14)	N4—C5—C6—C8	−179.72 (17)
C7—N3—N4—C5	0.00 (18)	C5—C6—C7—N3	0.21 (18)
N4—N3—C1—N1	−179.93 (15)	C5—C6—C7—N5	−179.42 (18)
N4—N3—C1—C2	0.6 (2)	C8—C6—C7—N3	179.73 (16)
C7—N3—C1—N1	−0.3 (3)	C8—C6—C7—N5	0.1 (3)
C7—N3—C1—C2	−179.69 (16)	C5—C6—C8—O1	−2.9 (3)
N4—N3—C7—N5	179.53 (15)	C5—C6—C8—O2	177.57 (18)
N4—N3—C7—C6	−0.13 (18)	C7—C6—C8—O1	177.73 (16)
C1—N3—C7—N5	−0.2 (3)	C7—C6—C8—O2	−1.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*A*···N1	0.86	2.17	2.775 (2)	127
N5—H5*B*···O2	0.86	2.40	2.942 (2)	122
N5—H5*B*···N2^{i}	0.86	2.41	3.017 (2)	128
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Symmetry codes: (i) −*x*+2, −*y*+1, −*z*; (ii) −*x*, −*y*+2, −*z*.