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5-Amino-1-(2-chlorophenyl)-1*H*-pyrazole-4-carbonitrile

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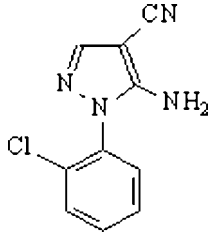
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.047; wR factor = 0.125; data-to-parameter ratio = 13.1.

In the title compound, $C_{10}H_7ClN_4$, the dihedral angle between the pyrazole and benzene ring planes is 69.48 (7)°. The crystal structure is stabilized by two N—H···N hydrogen bonds.

Related literature

For related literature, see: Campbell (1986); Cheng & Robins (1956); Holla *et al.* (2006).



Experimental

Crystal data

$C_{10}H_7ClN_4$
M_r = 218.65
Monoclinic, $P2_1/n$
a = 11.2005 (10) Å
b = 8.8432 (8) Å
c = 11.6970 (11) Å
β = 114.666 (1)°
V = 1052.85 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.33 mm^{-1}
T = 298 (2) K
0.42 × 0.31 × 0.23 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.873, T_{max} = 0.927
5334 measured reflections
1855 independent reflections
1625 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.125
S = 1.06
1855 reflections
142 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···N2^{i}	0.850 (9)	2.328 (12)	3.154 (3)	164 (2)
N3—H3B···N4^{ii}	0.850 (9)	2.307 (11)	3.147 (3)	170 (2)

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

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); 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, 2002); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2153).

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supplementary materials

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5-Amino-1-(2-chlorophenyl)-1*H*-pyrazole-4-carbonitrile

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Comment

The title compound, (Fig 1), is an important starting material for the synthesis of 1-(2-chlorophenyl)-4-substituted pyrazolo[3,4-*d*]pyrimidine, which is a potential purine antagonist (Cheng & Robins, 1956). The dihedral angle between the planar pyrazole and benzene ring is 69.48 (7)°. In the crystal packing, Fig. 2, there are two kinds of N—H—N hydrogen bonds; one to the cyano nitrogen and a second to one of the pyrazol ring N atoms.

Experimental

o-Chloroaniline (5 mmol) was dissolved in concentrated hydrochloric acid (2.5 ml), then the system was cooled with an ice bath, and kept at a temperature between 273k-278k. Sodium nitrate (5.12 mmol) was then slowly added in a dropwise fashion and the mixture was stirred for 30 min. The resulting diazonium salt was added dropwise into a solution of hydrochloric acid and stannous chloride (10 mmol). After stirring for 1 h stirring, sodium hydroxide was used to neutralize the solution to a PH = 7–8. Following the methods of Holla *et al.*(2006) and Campbell (1986), ethoxymethylenemalononitrile (5 mmol) was then added, appended ethanol as solvent, and refluxed for 1 h followed by filtration and washing several times with acetone, The organic solvent was distilled off, then the solution was filtered again to get the title compound (I) as a solid product (total yield of 81%). Colourless single crystals suitable for X-ray analysis were obtained by slow evaporation of an anhydrous ethanol-acetone (2:1) solution of (I)(m.p. 397 K). ^{1}H NMR (C_DCl_3, δ, p.p.m.): 4.57(s, 2H), 7.45(m, 3H), 7.57(d, 1H), 7.65(s, 1H).; ^{13}C NMR (C_DCl_3, δ, p.p.m.): 127.6 (1 C), 130.4 (1 C), 133.4 (1 C), 119.1 (1 C), 112.8 (1 C), 143.6 (1 C), 151.9 (1 C), 72.3 (1 C), 115.4 (1 C), 152.0 (1 C).

Refinement

All H atoms were initially located in a difference Fourier map but were eventually placed in their geometrically idealized positions and constrained to ride on their parent atoms, with N—H = 0.85 (2) Å and C—H = 0.93 Å, and with U_{iso}(H) = 1.2$_{eq}$(C,*N*).

Figures

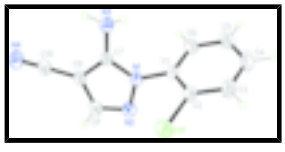
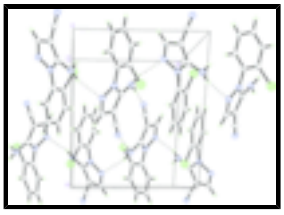


Figure 1 The molecular structure of (I) showing the atom numbering scheme and displacement ellipsoids at 50% probability level.



5-Amino-1-(2-chlorophenyl)-1*H*-pyrazole-4-carbonitrile

Crystal data

$C_{10}H_7ClN_4$	F_{000} = 448
M_r = 218.65	D_x = 1.379 Mg m^{-3}
Monoclinic, $P2_1/n$	Melting point: 397 K
Hall symbol: -P 2yn	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 11.2005 (10) Å	Cell parameters from 2518 reflections
b = 8.8432 (8) Å	θ = 3.0–24.9º
c = 11.6970 (11) Å	μ = 0.33 mm^{-1}
β = 114.6660 (10)º	T = 298 (2) K
V = 1052.85 (17) Å^3	Block, colorless
Z = 4	0.42 × 0.31 × 0.23 mm

Data collection

Bruker APEX area-detector diffractometer	1855 independent reflections
Radiation source: fine-focus sealed tube	1625 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.016
T = 298(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	h = −13→8
T_{min} = 0.873, T_{max} = 0.927	k = −10→9
5334 measured reflections	l = −13→13

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.047	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.125	$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.3491P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max}$ = 0.002
1855 reflections	$\Delta\rho_{max}$ = 0.17 e Å^{-3}

142 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}
3 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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}
Cl1	0.67558 (6)	0.49111 (8)	0.01439 (6)	0.0744 (3)
N1	0.69800 (15)	0.6722 (2)	0.23917 (15)	0.0495 (4)
N2	0.60604 (16)	0.7705 (2)	0.15579 (16)	0.0574 (5)
N3	0.73237 (18)	0.5163 (2)	0.41531 (18)	0.0559 (5)
N4	0.3825 (2)	0.6163 (3)	0.4018 (2)	0.0893 (8)
C1	0.81807 (18)	0.6483 (2)	0.22720 (18)	0.0478 (5)
C2	0.8178 (2)	0.5725 (3)	0.12405 (18)	0.0542 (5)
C3	0.9322 (2)	0.5576 (4)	0.1087 (2)	0.0784 (8)
H3	0.9316	0.5078	0.0384	0.094*
C4	1.0475 (2)	0.6159 (4)	0.1966 (3)	0.0829 (8)
H4	1.1246	0.6064	0.1855	0.099*
C5	1.0490 (2)	0.6879 (3)	0.3005 (2)	0.0703 (7)
H5	1.1276	0.7256	0.3608	0.084*
C6	0.9347 (2)	0.7047 (3)	0.3161 (2)	0.0596 (6)
H6	0.9360	0.7542	0.3868	0.072*
C7	0.65749 (18)	0.6105 (2)	0.32239 (17)	0.0453 (5)
C8	0.53318 (19)	0.6713 (2)	0.29280 (19)	0.0496 (5)
C9	0.50854 (19)	0.7673 (3)	0.1899 (2)	0.0562 (6)
H9	0.4315	0.8225	0.1503	0.067*
C10	0.4498 (2)	0.6396 (3)	0.3535 (2)	0.0602 (6)
H3A	0.7891 (19)	0.463 (2)	0.403 (2)	0.072*
H3B	0.694 (2)	0.475 (2)	0.456 (2)	0.072*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0615 (4)	0.0945 (5)	0.0607 (4)	−0.0166 (3)	0.0190 (3)	−0.0154 (3)
N1	0.0382 (8)	0.0673 (11)	0.0470 (9)	0.0038 (8)	0.0216 (7)	0.0056 (8)

N2	0.0451 (9)	0.0717 (12)	0.0545 (10)	0.0064 (9)	0.0198 (8)	0.0118 (9)
N3	0.0499 (10)	0.0729 (12)	0.0563 (11)	0.0114 (9)	0.0332 (9)	0.0117 (9)
N4	0.0585 (12)	0.133 (2)	0.0959 (16)	0.0179 (13)	0.0512 (12)	0.0255 (15)
C1	0.0394 (10)	0.0623 (12)	0.0467 (10)	0.0009 (9)	0.0229 (8)	0.0049 (9)
C2	0.0479 (12)	0.0732 (14)	0.0453 (11)	−0.0076 (10)	0.0232 (9)	−0.0019 (10)
C3	0.0616 (15)	0.124 (2)	0.0647 (15)	−0.0091 (15)	0.0414 (13)	−0.0199 (15)
C4	0.0511 (14)	0.129 (2)	0.0846 (18)	−0.0084 (14)	0.0439 (13)	−0.0108 (17)
C5	0.0413 (12)	0.0935 (18)	0.0734 (15)	−0.0097 (12)	0.0211 (11)	−0.0098 (13)
C6	0.0472 (12)	0.0777 (15)	0.0544 (12)	−0.0019 (11)	0.0216 (10)	−0.0099 (11)
C7	0.0386 (10)	0.0564 (11)	0.0441 (10)	−0.0018 (9)	0.0205 (8)	−0.0052 (9)
C8	0.0384 (10)	0.0610 (12)	0.0531 (11)	−0.0020 (9)	0.0228 (8)	−0.0036 (9)
C9	0.0386 (11)	0.0692 (14)	0.0595 (12)	0.0048 (10)	0.0191 (9)	0.0030 (10)
C10	0.0415 (11)	0.0777 (15)	0.0655 (13)	0.0058 (10)	0.0264 (10)	0.0040 (11)

Geometric parameters (Å, °)

Cl1—C2	1.731 (2)	C3—C4	1.372 (4)
N1—C7	1.349 (2)	C3—H3	0.9300
N1—N2	1.389 (2)	C4—C5	1.365 (4)
N1—C1	1.425 (2)	C4—H4	0.9300
N2—C9	1.310 (3)	C5—C6	1.376 (3)
N3—C7	1.348 (3)	C5—H5	0.9300
N3—H3A	0.850 (9)	C6—H6	0.9300
N3—H3B	0.850 (9)	C7—C8	1.395 (3)
N4—C10	1.134 (3)	C8—C9	1.403 (3)
C1—C2	1.379 (3)	C8—C10	1.416 (3)
C1—C6	1.379 (3)	C9—H9	0.9300
C2—C3	1.372 (3)		
C7—N1—N2	112.69 (15)	C3—C4—H4	120.0
C7—N1—C1	128.77 (16)	C4—C5—C6	120.1 (2)
N2—N1—C1	118.54 (15)	C4—C5—H5	119.9
C9—N2—N1	103.91 (16)	C6—C5—H5	119.9
C7—N3—H3A	117.9 (16)	C5—C6—C1	120.1 (2)
C7—N3—H3B	115.3 (16)	C5—C6—H6	119.9
H3A—N3—H3B	116.5 (16)	C1—C6—H6	119.9
C2—C1—C6	119.41 (18)	N3—C7—N1	123.25 (17)
C2—C1—N1	120.06 (17)	N3—C7—C8	131.22 (18)
C6—C1—N1	120.50 (18)	N1—C7—C8	105.46 (17)
C3—C2—C1	120.0 (2)	C7—C8—C9	105.35 (17)
C3—C2—Cl1	118.93 (18)	C7—C8—C10	126.7 (2)
C1—C2—Cl1	121.02 (15)	C9—C8—C10	127.92 (19)
C2—C3—C4	120.2 (2)	N2—C9—C8	112.58 (18)
C2—C3—H3	119.9	N2—C9—H9	123.7
C4—C3—H3	119.9	C8—C9—H9	123.7
C5—C4—C3	120.1 (2)	N4—C10—C8	179.0 (3)
C5—C4—H4	120.0		
C7—N1—N2—C9	−0.1 (2)	C2—C1—C6—C5	1.3 (3)
C1—N1—N2—C9	179.50 (18)	N1—C1—C6—C5	−176.6 (2)
C7—N1—C1—C2	111.1 (2)	N2—N1—C7—N3	−177.35 (19)

N2—N1—C1—C2	−68.4 (3)	C1—N1—C7—N3	3.1 (3)
C7—N1—C1—C6	−71.1 (3)	N2—N1—C7—C8	−0.2 (2)
N2—N1—C1—C6	109.5 (2)	C1—N1—C7—C8	−179.70 (19)
C6—C1—C2—C3	−1.9 (4)	N3—C7—C8—C9	177.2 (2)
N1—C1—C2—C3	176.0 (2)	N1—C7—C8—C9	0.4 (2)
C6—C1—C2—Cl1	176.53 (18)	N3—C7—C8—C10	−3.7 (4)
N1—C1—C2—Cl1	−5.6 (3)	N1—C7—C8—C10	179.4 (2)
C1—C2—C3—C4	1.0 (4)	N1—N2—C9—C8	0.3 (2)
Cl1—C2—C3—C4	−177.5 (2)	C7—C8—C9—N2	−0.4 (3)
C2—C3—C4—C5	0.6 (5)	C10—C8—C9—N2	−179.5 (2)
C3—C4—C5—C6	−1.2 (5)	C7—C8—C10—N4	145 (16)
C4—C5—C6—C1	0.3 (4)	C9—C8—C10—N4	−36 (16)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3A···N2^{i}	0.850 (9)	2.328 (12)	3.154 (3)	164 (2)
N3—H3B···N4^{ii}	0.850 (9)	2.307 (11)	3.147 (3)	170 (2)

Symmetry codes: (i) −*x*+3/2, *y*−1/2, −*z*+1/2; (ii) −*x*+1, −*y*+1, −*z*+1.

Fig. 1

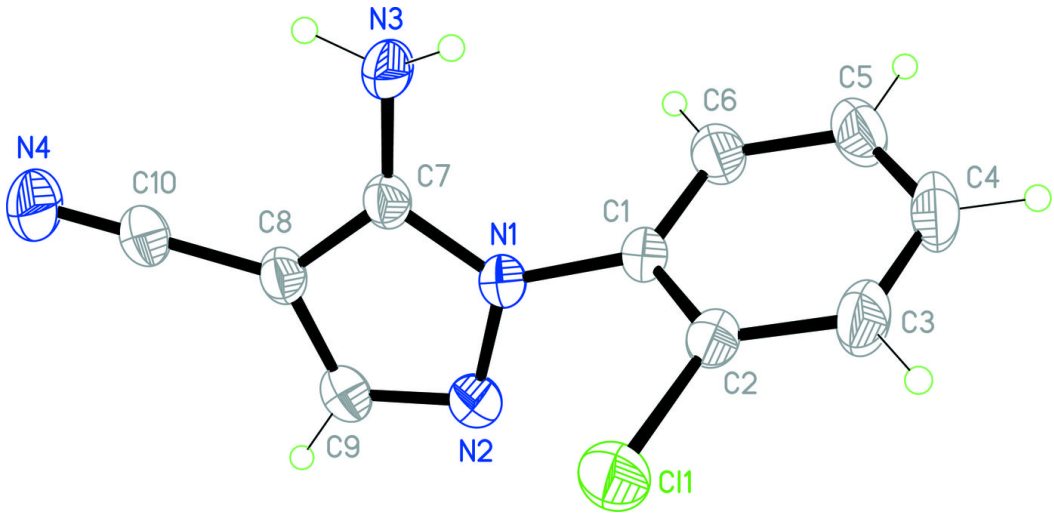


Fig. 2