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5-Amino-1-(2,6-dichloro-4-nitrophenyl)-pyrazole-3-carbonitrile

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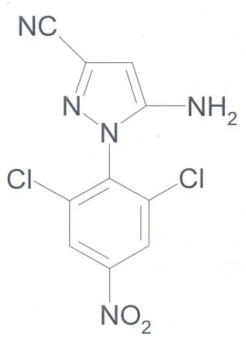
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.058; wR factor = 0.144; data-to-parameter ratio = 12.4.

In the title compound, $C_{10}H_5Cl_2N_5O_2$, the dihedral angle between the pyrazole and benzene ring planes is 80.59 (12)°. The crystal structure is stabilized by N—H···N and N—H···O hydrogen bonds.

Related literature

For related literature, see: Clavel *et al.* (2003); Hatton *et al.* (1993); Hainzl & Casida (1996); Zhong *et al.* (2005).



Experimental

Crystal data

$C_{10}H_5Cl_2N_5O_2$
M_r = 298.09
Monoclinic, $C2/c$
a = 13.1756 (13) Å
b = 10.5514 (13) Å
c = 18.0297 (19) Å
β = 91.356 (3)°
V = 2505.8 (5) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.52 mm^{-1}
T = 298 (2) K
0.38 × 0.22 × 0.18 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.826, T_{max} = 0.912
6435 measured reflections
2211 independent reflections
1902 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.144
S = 1.12
2211 reflections
178 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···O1^{i}	0.837 (16)	2.37 (2)	3.154 (4)	156 (3)
N5—H5B···N4^{ii}	0.844 (16)	2.526 (19)	3.253 (4)	145 (3)
N5—H5B···N4^{iii}	0.844 (16)	2.58 (3)	3.166 (4)	128 (2)

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

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: OM2155).

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supplementary materials

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5-Amino-1-(2,6-dichloro-4-nitrophenyl)pyrazole-3-carbonitrile

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Comment

The molecular structure of the title compound is similar to 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)pyrazole, an important starting material for the insecticide fipronil (Clavel *et al.*, 2003; Hatton *et al.*, 1993). The molecule is shown in Fig. 1. It contains two essentially planar rings. The dihedral angle between the pyrazole and benzene ring planes is 80.59 (12)°.

Experimental

A suspension of nitrosyl sulfuric acid prepared from sodium nitrite (0.055 mol) and concentrated sulfuric acid (1.5 ml) was diluted with acetic acid (5 ml), cooled to 283 K, and stirred mechanically. To this was added a solution of 2,6-dichloro-4-nitroaniline (0.05 mol) in acetic acid (20 ml) dropwise over 15 minutes at room temperature. This mixture was heated to 335 K for 20 minutes and poured onto a stirred solution of ethyl 2,3-dicyanopropionate (0.05 mol) in acetic acid (10 ml) and water (30 ml) at room temperature. After 15 minutes, water (20 ml) was added, and the oily layer separated. The aqueous solution was then extracted with dichloromethane (30 ml) and the extracts combined with the oil and washed with ammonia solution (to pH=9). The organic phase was then stirred with ammonia (5 ml) for 2 h, and the dichloromethane layer then separated. This was washed with water (30 ml), 1 N hydrochloric acid (30 ml), dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to give an oily solid. Crytstallization from ethanol-acetone gave the title compound. Total yield was 81%. Yellow single crystals suitable for X-ray analysis were obtained by slow evaporation of an anhydrous ethanol-acetone (2:1) solution. ^{1}H NMR (CD_3COCD_3, δ, p.p.m.): 8.51 (s,2*H*), 6.07 (s,1*H*), 5.84 (s,2*H*).; ^{13}C NMR (CD_3COCD_3, δ, p.p.m.): 149.2, 148.7, 137.6, 136.2, 131.0, 126.8, 123.7, 113.6, 91.28

Refinement

The two H atoms of the N5 atom were located from difference-density maps and refined with N—H and H···H distances restrained to be 0.85±0.02 Å and 1.45±0.01 Å, respectively, and with U_{iso} = 1.2U_{eq}(parent atom). The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of Csp^2—H = 0.93 Å with U_{iso} = 1.2U_{eq}(parent atom).

Figures

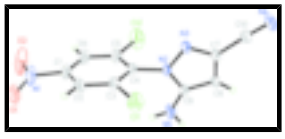

Fig. 1. The molecular structure showing the atom numbering scheme and displacement ellipsoids at the 50% probability level. Hydrogen atoms are shown as spheres of an arbitrary size.

5-Amino-1-(2,6-dichloro-4-nitrophenyl)pyrazole-3-carbonitrile

Crystal data

$C_{10}H_5Cl_2N_5O_2$	F_{000} = 1200
M_r = 298.09	D_x = 1.580 Mg m^{-3}
Monoclinic, *C*2/*c*	Melting point: 473 K
Hall symbol: -C 2yc	Mo *K*α radiation λ = 0.71073 Å
a = 13.1756 (13) Å	Cell parameters from 2235 reflections
b = 10.5514 (13) Å	θ = 2.5–24.8º
c = 18.0297 (19) Å	μ = 0.52 mm^{-1}
β = 91.356 (3)º	*T* = 298 (2) K
V = 2505.8 (5) Å^3	Block, colorless
Z = 8	0.38 × 0.22 × 0.18 mm

Data collection

Bruker APEX area-detector diffractometer	2211 independent reflections
Radiation source: fine-focus sealed tube	1902 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.026
T = 298(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.3º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	*h* = −15→13
T_{min} = 0.826, T_{max} = 0.912	*k* = −12→7
6435 measured reflections	*l* = −21→20

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.058	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.144	$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 3.910P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.12	$(\Delta/\sigma)_{max}$ = 0.001
2211 reflections	$\Delta\rho_{max}$ = 0.31 e Å^{-3}
178 parameters	$\Delta\rho_{min}$ = −0.22 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	−0.08877 (7)	0.03784 (11)	0.32992 (5)	0.0741 (4)
Cl2	0.11826 (9)	0.31258 (15)	0.53159 (6)	0.1012 (5)
O1	−0.3095 (2)	0.0874 (3)	0.5636 (2)	0.0915 (11)
O2	−0.2151 (3)	0.1648 (3)	0.6505 (2)	0.1226 (15)
N1	−0.2305 (3)	0.1292 (3)	0.5878 (2)	0.0732 (10)
N2	0.07792 (16)	0.2094 (2)	0.38293 (12)	0.0389 (6)
N3	0.15519 (17)	0.1271 (2)	0.36863 (13)	0.0409 (6)
N4	0.3713 (2)	0.1004 (3)	0.26417 (18)	0.0640 (8)
N5	0.0188 (2)	0.4179 (3)	0.35515 (18)	0.0650 (9)
H5A	−0.0377 (17)	0.394 (3)	0.3703 (17)	0.055*
H5B	0.021 (2)	0.481 (2)	0.3264 (16)	0.055*
C1	−0.1449 (3)	0.1407 (3)	0.53566 (19)	0.0516 (8)
C2	−0.1559 (2)	0.0850 (3)	0.4670 (2)	0.0521 (8)
H2	−0.2125	0.0359	0.4548	0.063*
C3	−0.0794 (2)	0.1046 (3)	0.41680 (16)	0.0440 (7)
C4	0.0038 (2)	0.1778 (3)	0.43599 (15)	0.0390 (7)
C5	0.0124 (2)	0.2279 (3)	0.50711 (17)	0.0512 (8)
C6	−0.0625 (3)	0.2094 (3)	0.55791 (18)	0.0582 (9)
H6	−0.0570	0.2427	0.6056	0.070*
C7	0.20940 (19)	0.1928 (3)	0.32125 (15)	0.0381 (7)
C8	0.1712 (2)	0.3121 (3)	0.30524 (16)	0.0441 (7)
H8	0.1980	0.3727	0.2738	0.053*
C9	0.0852 (2)	0.3210 (3)	0.34607 (16)	0.0411 (7)
C10	0.3002 (2)	0.1386 (3)	0.29029 (17)	0.0457 (7)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0674 (6)	0.1008 (8)	0.0544 (5)	−0.0178 (5)	0.0048 (4)	−0.0114 (5)
Cl2	0.0827 (8)	0.1520 (13)	0.0691 (7)	−0.0495 (8)	0.0077 (5)	−0.0275 (7)
O1	0.0604 (17)	0.083 (2)	0.133 (3)	0.0106 (16)	0.0556 (18)	0.0401 (19)
O2	0.169 (4)	0.103 (3)	0.101 (3)	−0.035 (2)	0.102 (3)	−0.031 (2)

N1	0.081 (2)	0.0444 (17)	0.097 (3)	0.0071 (17)	0.058 (2)	0.0161 (18)
N2	0.0303 (11)	0.0462 (14)	0.0410 (13)	0.0048 (11)	0.0171 (10)	0.0092 (11)
N3	0.0336 (12)	0.0446 (14)	0.0451 (13)	0.0059 (11)	0.0134 (10)	0.0073 (11)
N4	0.0459 (16)	0.0627 (19)	0.085 (2)	0.0149 (14)	0.0321 (15)	0.0002 (16)
N5	0.0541 (17)	0.0606 (19)	0.082 (2)	0.0221 (15)	0.0395 (16)	0.0264 (16)
C1	0.0544 (19)	0.0429 (17)	0.059 (2)	0.0120 (16)	0.0341 (16)	0.0148 (16)
C2	0.0373 (16)	0.0468 (18)	0.073 (2)	−0.0015 (14)	0.0162 (15)	0.0138 (16)
C3	0.0388 (16)	0.0491 (18)	0.0445 (16)	0.0020 (14)	0.0106 (12)	0.0096 (14)
C4	0.0333 (14)	0.0444 (16)	0.0397 (15)	0.0064 (13)	0.0115 (12)	0.0094 (13)
C5	0.0479 (17)	0.062 (2)	0.0443 (17)	−0.0040 (16)	0.0131 (14)	0.0003 (15)
C6	0.071 (2)	0.061 (2)	0.0433 (18)	0.0038 (19)	0.0199 (16)	0.0036 (16)
C7	0.0305 (14)	0.0446 (16)	0.0395 (15)	0.0035 (12)	0.0109 (11)	−0.0005 (13)
C8	0.0403 (15)	0.0450 (17)	0.0480 (17)	0.0046 (14)	0.0198 (13)	0.0087 (14)
C9	0.0349 (14)	0.0460 (17)	0.0431 (16)	0.0069 (13)	0.0143 (12)	0.0066 (14)
C10	0.0421 (17)	0.0447 (17)	0.0507 (17)	0.0034 (14)	0.0128 (14)	0.0044 (14)

Geometric parameters (Å, °)

Cl1—C3	1.719 (3)	C1—C6	1.358 (5)
Cl2—C5	1.706 (3)	C1—C2	1.374 (5)
O1—N1	1.203 (5)	C2—C3	1.386 (4)
O2—N1	1.204 (5)	C2—H2	0.9300
N1—C1	1.489 (4)	C3—C4	1.378 (4)
N2—C9	1.357 (4)	C4—C5	1.389 (4)
N2—N3	1.367 (3)	C5—C6	1.377 (4)
N2—C4	1.423 (3)	C6—H6	0.9300
N3—C7	1.323 (4)	C7—C8	1.383 (4)
N4—C10	1.133 (4)	C7—C10	1.449 (4)
N5—C9	1.358 (4)	C8—C9	1.369 (4)
N5—H5A	0.837 (16)	C8—H8	0.9300
N5—H5B	0.844 (16)		
O1—N1—O2	125.4 (3)	C3—C4—C5	119.5 (3)
O1—N1—C1	117.6 (4)	C3—C4—N2	121.1 (3)
O2—N1—C1	117.0 (4)	C5—C4—N2	119.3 (3)
C9—N2—N3	113.4 (2)	C6—C5—C4	121.0 (3)
C9—N2—C4	126.2 (2)	C6—C5—Cl2	119.8 (3)
N3—N2—C4	120.3 (2)	C4—C5—Cl2	119.1 (2)
C7—N3—N2	101.8 (2)	C1—C6—C5	117.4 (3)
C9—N5—H5A	113 (2)	C1—C6—H6	121.3
C9—N5—H5B	119 (2)	C5—C6—H6	121.3
H5A—N5—H5B	119 (2)	N3—C7—C8	114.4 (2)
C6—C1—C2	124.1 (3)	N3—C7—C10	120.3 (3)
C6—C1—N1	118.0 (3)	C8—C7—C10	125.3 (3)
C2—C1—N1	117.9 (3)	C9—C8—C7	104.6 (3)
C1—C2—C3	117.5 (3)	C9—C8—H8	127.7
C1—C2—H2	121.3	C7—C8—H8	127.7
C3—C2—H2	121.3	N2—C9—N5	122.7 (2)
C4—C3—C2	120.4 (3)	N2—C9—C8	105.8 (2)
C4—C3—Cl1	119.8 (2)	N5—C9—C8	131.3 (3)

C2—C3—Cl1	119.8 (3)	N4—C10—C7	177.2 (3)
C9—N2—N3—C7	−0.4 (3)	N2—C4—C5—C6	173.9 (3)
C4—N2—N3—C7	−176.3 (3)	C3—C4—C5—Cl2	177.2 (2)
O1—N1—C1—C6	167.6 (3)	N2—C4—C5—Cl2	−6.6 (4)
O2—N1—C1—C6	−11.1 (5)	C2—C1—C6—C5	2.6 (5)
O1—N1—C1—C2	−10.1 (5)	N1—C1—C6—C5	−174.9 (3)
O2—N1—C1—C2	171.2 (3)	C4—C5—C6—C1	−0.1 (5)
C6—C1—C2—C3	−2.5 (5)	Cl2—C5—C6—C1	−179.6 (3)
N1—C1—C2—C3	175.0 (3)	N2—N3—C7—C8	0.4 (3)
C1—C2—C3—C4	−0.1 (5)	N2—N3—C7—C10	−179.2 (3)
C1—C2—C3—Cl1	−179.8 (2)	N3—C7—C8—C9	−0.3 (4)
C2—C3—C4—C5	2.5 (5)	C10—C7—C8—C9	179.3 (3)
Cl1—C3—C4—C5	−177.9 (2)	N3—N2—C9—N5	−176.9 (3)
C2—C3—C4—N2	−173.7 (3)	C4—N2—C9—N5	−1.3 (5)
Cl1—C3—C4—N2	6.0 (4)	N3—N2—C9—C8	0.2 (3)
C9—N2—C4—C3	100.3 (4)	C4—N2—C9—C8	175.8 (3)
N3—N2—C4—C3	−84.4 (3)	C7—C8—C9—N2	0.1 (3)
C9—N2—C4—C5	−75.9 (4)	C7—C8—C9—N5	176.8 (3)
N3—N2—C4—C5	99.5 (3)	N3—C7—C10—N4	171 (7)
C3—C4—C5—C6	−2.4 (5)	C8—C7—C10—N4	−8(8)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5A···O1^{i}	0.837 (16)	2.37 (2)	3.154 (4)	156 (3)
N5—H5B···N4^{ii}	0.844 (16)	2.526 (19)	3.253 (4)	145 (3)
N5—H5B···N4^{iii}	0.844 (16)	2.58 (3)	3.166 (4)	128 (2)

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

Fig. 1