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# 3-Chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridazine

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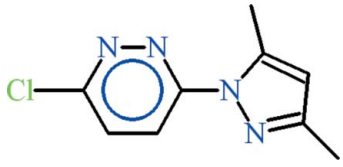
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.031; $wR$ factor = 0.090; data-to-parameter ratio = 13.4.

In the title compound, $C_9H_9ClN_4$, the dihedral angle between the aromatic rings is 6.25 (9)°. The whole molecule is approximately planar (r.m.s. deviation = 0.070 Å). In the crystal, $\pi$–$\pi$ interactions between the centroids of the pyridazine rings [separation = 3.5904 (10) Å] occur.

## Related literature

For background to pyrazolylpyridazine derivatives and for related crystal structures, see: Ather *et al.* (2010*a*,*b*,*c*). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).



## Experimental

### *Crystal data*

$C_9H_9ClN_4$
$M_r$ = 208.65
Monoclinic, $P2_1/c$
$a$ = 11.2773 (3) Å
$b$ = 8.4181 (2) Å
$c$ = 11.3501 (3) Å
$\beta$ = 116.529 (1)°
$V$ = 964.05 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.36 mm$^{-1}$
$T$ = 296 K
0.32 × 0.24 × 0.20 mm

### *Data collection*

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min}$ = 0.903, $T_{max}$ = 0.932
6922 measured reflections
1727 independent reflections
1514 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.022

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.090
$S$ = 1.04
1727 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.19 e Å$^{-3}$

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: HB5625).

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# supporting information

*Acta Cryst.* (2010). E**66**, o2493 [doi:10.1107/S1600536810034756]

## 3-Chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridazine

**Abdul Qayyum Ather, M. Nawaz Tahir, Misbahul Ain Khan, Muhammad Makshoof Athar and Eliana Aparecida Silicz Bueno**

### 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 the title compound, the 3-chloro-pyridazine group A (C1—C4/N1/N2/CL1) and 3,5-dimethyl-pyrazol moiety B (N3/N4/C5—C9) are planar with r. m. s. deviation of 0.0057 and 0.0121 Å, respectively. The dihedral angle between A/B is 6.40 (9)°. The title compound essentially consists of monomers. The molecules are stabilized due to $\pi$–$\pi$ interactions. There exist $\pi$–$\pi$ interactions between the centroids of pyridazine rings at a distance of 3.5904 (10) Å [symmetry code: 1 - *x*, 1 - *y*, 1 - *z*]. The centroids of pyridazine and pyrazol rings are separated at 4.1319 (9) Å [symmetry code: 1 - *x*, 1 - *y*, 1 - *z*] and 4.4233 (9)Å [symmetry code: 1 - *x*, 2 - *y*, 1 - *z*].

### S2. Experimental

3-Chloro-6-hydrazinylpyridazine (1 g, 6.92 mmol) was dissolved in 5 ml of ethanol. To this solution acetylacetone (8 mmol) and acetic acid (0.7 ml) were added and heated for 30 min. The unreacted acetic acid was removed under vacuum and charged to 25 ml of distilled water and filtered. The final product was re-crystallized in ethanol to obtain colourless prisms of (I).

### S3. Refinement

The H-atoms were positioned geometrically (C–H = 0.93–0.96 Å) and were included in the refinement in the riding model approximation, with $U_{iso}$(H) = x$U_{eq}$(C), where x = 1.5 for methyl and x = 1.2 for aryl H-atoms.

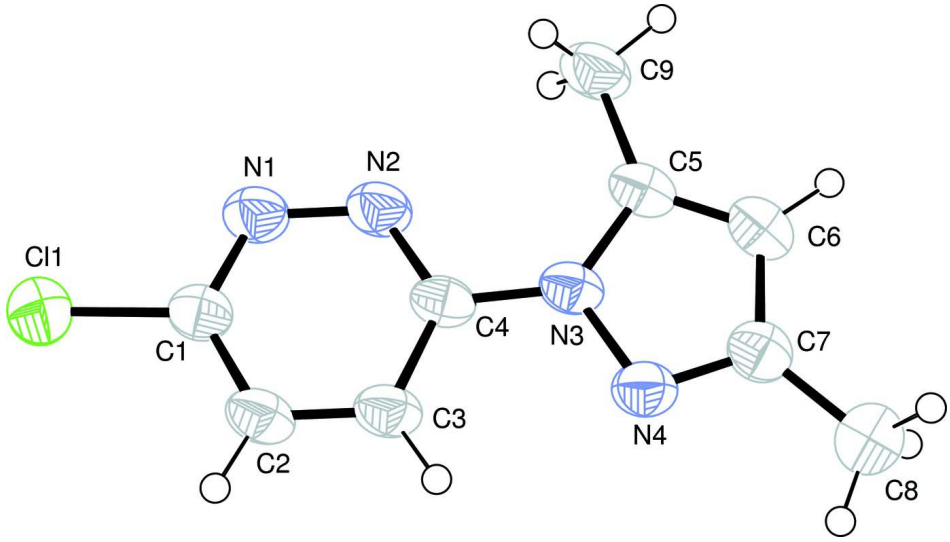


**Figure 1**

View of the title compound with displacement ellipsoids drawn at the 50% probability level. H-atoms are shown as small spheres of arbitrary radius.

### 3-Chloro-6-(3,5-dimethyl-1*H*-pyrazol-1-yl)pyridazine

*Crystal data*

$C_9H_9ClN_4$
$M_r = 208.65$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 11.2773$ (3) Å
$b = 8.4181$ (2) Å
$c = 11.3501$ (3) Å
$\beta = 116.529$ (1)°
$V = 964.05$ (4) Å$^3$
$Z = 4$
$F(000) = 432$
$D_x = 1.438$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1514 reflections
$\theta = 3.1$–25.3°
$\mu = 0.36$ mm$^{-1}$
$T = 296$ K
Prism, colourless
0.32 × 0.24 × 0.20 mm

*Data collection*

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.10 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.903$, $T_{max} = 0.932$
6922 measured reflections
1727 independent reflections
1514 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.3°$, $\theta_{min} = 3.1°$
$h = -13\rightarrow13$
$k = -10\rightarrow10$
$l = -13\rightarrow13$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.090$
$S = 1.04$
1727 reflections
129 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
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.3389P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å$^{-3}$
$\Delta\rho_{min} = -0.19$ 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 | 0.76089 (4) | 0.97122 (6) | 0.60328 (4) | 0.0581 (2) |
| N1 | 0.56592 (14) | 0.81330 (18) | 0.60486 (13) | 0.0495 (5) |
| N2 | 0.45739 (14) | 0.71964 (18) | 0.55421 (13) | 0.0487 (5) |
| N3 | 0.29683 (12) | 0.57550 (16) | 0.38434 (12) | 0.0419 (4) |
| N4 | 0.25369 (14) | 0.50746 (16) | 0.26163 (13) | 0.0465 (4) |
| C1 | 0.62272 (15) | 0.84978 (19) | 0.53015 (15) | 0.0427 (5) |
| C2 | 0.58063 (16) | 0.7982 (2) | 0.40156 (16) | 0.0480 (5) |
| C3 | 0.47217 (16) | 0.7034 (2) | 0.35066 (15) | 0.0460 (5) |
| C4 | 0.41180 (14) | 0.66847 (18) | 0.43182 (14) | 0.0389 (5) |
| C5 | 0.21463 (16) | 0.5362 (2) | 0.44074 (16) | 0.0449 (5) |
| C6 | 0.11915 (17) | 0.4428 (2) | 0.35130 (17) | 0.0510 (6) |
| C7 | 0.14674 (16) | 0.4269 (2) | 0.24272 (16) | 0.0464 (5) |
| C8 | 0.07365 (19) | 0.3310 (3) | 0.12074 (19) | 0.0620 (7) |
| C9 | 0.23144 (19) | 0.5897 (3) | 0.57258 (17) | 0.0589 (6) |
| H2 | 0.62480 | 0.82738 | 0.35258 | 0.0576* |
| H3 | 0.43929 | 0.66322 | 0.26555 | 0.0551* |
| H6 | 0.04831 | 0.39741 | 0.36007 | 0.0612* |
| H8A | 0.11672 | 0.34089 | 0.06480 | 0.0930* |
| H8B | −0.01582 | 0.36889 | 0.07498 | 0.0930* |
| H8C | 0.07304 | 0.22143 | 0.14400 | 0.0930* |
| H9A | 0.15789 | 0.55308 | 0.58622 | 0.0883* |
| H9B | 0.23501 | 0.70358 | 0.57665 | 0.0883* |
| H9C | 0.31225 | 0.54673 | 0.63974 | 0.0883* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0593 (3) | 0.0588 (3) | 0.0592 (3) | −0.0085 (2) | 0.0291 (2) | −0.0040 (2) |
| N1 | 0.0543 (8) | 0.0585 (9) | 0.0412 (7) | −0.0008 (7) | 0.0264 (6) | −0.0005 (6) |
| N2 | 0.0513 (8) | 0.0624 (9) | 0.0396 (7) | −0.0016 (7) | 0.0268 (6) | 0.0009 (6) |
| N3 | 0.0427 (7) | 0.0509 (8) | 0.0372 (7) | 0.0059 (6) | 0.0223 (6) | 0.0047 (6) |
| N4 | 0.0480 (8) | 0.0545 (8) | 0.0410 (7) | 0.0031 (6) | 0.0234 (6) | −0.0009 (6) |
| C1 | 0.0446 (8) | 0.0435 (8) | 0.0429 (9) | 0.0066 (7) | 0.0222 (7) | 0.0050 (7) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0487 (9) | 0.0617 (10) | 0.0422 (9) | 0.0029 (8) | 0.0280 (7) | 0.0064 (7) |
| C3 | 0.0471 (9) | 0.0607 (10) | 0.0356 (8) | 0.0041 (7) | 0.0234 (7) | 0.0025 (7) |
| C4 | 0.0408 (8) | 0.0433 (8) | 0.0369 (8) | 0.0105 (6) | 0.0213 (6) | 0.0084 (6) |
| C5 | 0.0443 (9) | 0.0525 (9) | 0.0456 (9) | 0.0093 (7) | 0.0269 (7) | 0.0098 (7) |
| C6 | 0.0443 (9) | 0.0581 (10) | 0.0564 (10) | 0.0033 (8) | 0.0277 (8) | 0.0084 (8) |
| C7 | 0.0438 (9) | 0.0474 (9) | 0.0484 (9) | 0.0069 (7) | 0.0209 (7) | 0.0053 (7) |
| C8 | 0.0608 (11) | 0.0638 (12) | 0.0592 (11) | −0.0047 (9) | 0.0249 (9) | −0.0061 (9) |
| C9 | 0.0569 (10) | 0.0818 (13) | 0.0511 (10) | −0.0020 (10) | 0.0360 (9) | 0.0010 (9) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cl1—C1 | 1.7340 (18) | C5—C9 | 1.492 (3) |
| N1—N2 | 1.350 (2) | C6—C7 | 1.406 (3) |
| N1—C1 | 1.307 (2) | C7—C8 | 1.493 (3) |
| N2—C4 | 1.320 (2) | C2—H2 | 0.9300 |
| N3—N4 | 1.3781 (18) | C3—H3 | 0.9300 |
| N3—C4 | 1.400 (2) | C6—H6 | 0.9300 |
| N3—C5 | 1.382 (2) | C8—H8A | 0.9600 |
| N4—C7 | 1.315 (2) | C8—H8B | 0.9600 |
| C1—C2 | 1.388 (2) | C8—H8C | 0.9600 |
| C2—C3 | 1.355 (3) | C9—H9A | 0.9600 |
| C3—C4 | 1.400 (2) | C9—H9B | 0.9600 |
| C5—C6 | 1.353 (2) | C9—H9C | 0.9600 |
| | | | |
| N2—N1—C1 | 118.35 (14) | C6—C7—C8 | 128.16 (18) |
| N1—N2—C4 | 119.46 (15) | C1—C2—H2 | 122.00 |
| N4—N3—C4 | 118.01 (14) | C3—C2—H2 | 122.00 |
| N4—N3—C5 | 111.21 (14) | C2—C3—H3 | 121.00 |
| C4—N3—C5 | 130.79 (13) | C4—C3—H3 | 121.00 |
| N3—N4—C7 | 105.27 (14) | C5—C6—H6 | 126.00 |
| Cl1—C1—N1 | 115.08 (12) | C7—C6—H6 | 126.00 |
| Cl1—C1—C2 | 120.01 (14) | C7—C8—H8A | 109.00 |
| N1—C1—C2 | 124.91 (16) | C7—C8—H8B | 109.00 |
| C1—C2—C3 | 116.90 (17) | C7—C8—H8C | 109.00 |
| C2—C3—C4 | 117.07 (15) | H8A—C8—H8B | 109.00 |
| N2—C4—N3 | 116.49 (15) | H8A—C8—H8C | 109.00 |
| N2—C4—C3 | 123.29 (16) | H8B—C8—H8C | 109.00 |
| N3—C4—C3 | 120.22 (13) | C5—C9—H9A | 109.00 |
| N3—C5—C6 | 105.38 (15) | C5—C9—H9B | 109.00 |
| N3—C5—C9 | 125.57 (16) | C5—C9—H9C | 109.00 |
| C6—C5—C9 | 129.05 (19) | H9A—C9—H9B | 109.00 |
| C5—C6—C7 | 107.42 (17) | H9A—C9—H9C | 109.00 |
| N4—C7—C6 | 110.72 (15) | H9B—C9—H9C | 109.00 |
| N4—C7—C8 | 121.10 (17) | | |
| | | | |
| C1—N1—N2—C4 | −0.2 (2) | C4—N3—C5—C6 | −179.65 (16) |
| N2—N1—C1—Cl1 | 179.72 (12) | C4—N3—C5—C9 | 0.8 (3) |
| N2—N1—C1—C2 | −0.6 (3) | N3—N4—C7—C6 | 0.49 (19) |

| | | | |
|---|---|---|---|
| N1—N2—C4—N3 | −178.28 (14) | N3—N4—C7—C8 | −177.82 (16) |
| N1—N2—C4—C3 | 1.5 (3) | Cl1—C1—C2—C3 | 179.88 (13) |
| C4—N3—N4—C7 | 179.37 (14) | N1—C1—C2—C3 | 0.2 (3) |
| C5—N3—N4—C7 | −0.21 (18) | C1—C2—C3—C4 | 0.9 (2) |
| N4—N3—C4—N2 | −173.89 (14) | C2—C3—C4—N2 | −1.8 (3) |
| N4—N3—C4—C3 | 6.4 (2) | C2—C3—C4—N3 | 177.92 (15) |
| C5—N3—C4—N2 | 5.6 (3) | N3—C5—C6—C7 | 0.43 (19) |
| C5—N3—C4—C3 | −174.15 (16) | C9—C5—C6—C7 | 179.98 (19) |
| N4—N3—C5—C6 | −0.15 (19) | C5—C6—C7—N4 | −0.6 (2) |
| N4—N3—C5—C9 | −179.73 (17) | C5—C6—C7—C8 | 177.56 (19) |