Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# 1-(3-Chloro-2-pyridyl)-3-methyl-1*H*-pyrazole-5-carboxylic acid

**Hua Cai,* Ying Guo, Jian-Gang Li and Yao Wu**

College of Science, Civil Aviation University of China, Tianjin 300300, People's Republic of China
Correspondence e-mail: caihua-1109@163.com

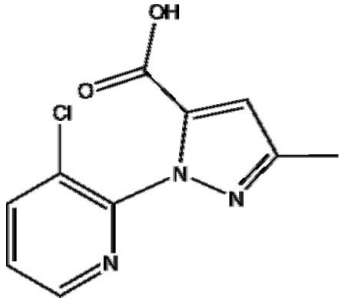
Received 18 October 2009; accepted 23 October 2009

Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.033; $wR$ factor = 0.075; data-to-parameter ratio = 13.2.

In the title molecule, $C_{10}H_8ClN_3O_2$, the dihedral angle between the pyridine and pyrazole rings is 64.01 (8)°. In the crystal structure, intermolecular O—H···N hydrogen bonds link molecules, forming extended chains along [001]. These chains are, in turn, linked by weak intermolecular C—H···O interactions, forming a two-dimensional network perpendicular to the *b* axis.

## Related literature

The title compound was prepared adventitiously as part of our research program related to metal-organic frameworks. See: Lehn (1995) for background information. For the topologies of metal-organic frameworks, see: Kitakawa *et al.* (2004); Rosi *et al.* (2005); Subramanian & Zaworotko (1994).




## Experimental

### *Crystal data*

$C_{10}H_8ClN_3O_2$
$M_r$ = 237.64
Orthorhombic, $Pca2_1$
$a$ = 8.250 (6) Å
$b$ = 11.232 (8) Å
$c$ = 11.942 (8) Å
$V$ = 1106.6 (13) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.33 mm$^{-1}$
$T$ = 296 K
0.24 × 0.20 × 0.18 mm

### *Data collection*

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.582, $T_{max}$ = 1.000
5084 measured reflections
1943 independent reflections
1754 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.032

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.075
$S$ = 1.04
1943 reflections
147 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.14 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.13 e Å$^{-3}$
Absolute structure: Flack (1983) 912 Friedel pairs
Flack parameter: 0.03 (7)

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2···N1$^{i}$ | 0.82 | 1.93 | 2.755 (3) | 180 |
| C2—H2$A$···O1$^{ii}$ | 0.93 | 2.36 | 3.258 (4) | 161 |

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

Data collection: *APEX2* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXTL*.

We acknowledge financial support by the Scientific Research Foundation of the Civil Aviation University of China (No. 08CAUC-S01) and the Natural Science Foundation of Tianjin (09JCYBJC04200).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2933).

## References

Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Kitakawa, S., Kitaura, T. & Noro, S. (2004). *Angew. Chem. Int. Ed.* **43**, 2334–2375.
Lehn, J. M. (1995). *Supramolecular Chemistry: Concepts and Perspectives*. New York: Wiley-VCH.
Rosi, N. L., Kim, J., Eddaoudi, M., Chen, B., O'Keeffe, M. & Yaghi, O. M. (2005). *J. Am. Chem. Soc.* **127**, 1504–1518.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Subramanian, S. & Zaworotko, M. J. (1994). *Coord. Chem. Rev.* **137**, 357–401.

# supplementary materials

*Acta Cryst.* (2009). E**65**, o2876 [ **doi:10.1107/S1600536809043906** ]

# 1-(3-Chloro-2-pyridyl)-3-methyl-1*H*-pyrazole-5-carboxylic acid

**H. Cai, Y. Guo, J.-G. Li and Y. Wu**

## Comment

Recently, metal-organic frameworks (MOFs) have attracted great attention (Lehn *et al.*, 1995) because of their intriguing topologies (Subramanian *et al.*, 1994; Kitakawa *et al.*, 2004; Rosi *et al.*, 2005). During our efforts to investigate the assembly of metal-organic coordination frameworks, a new compound, (I), was accidentally generated under hydrothermal conditions and the crystal structure of the title compound (I) is described in this paper. The molecular structure of (I) is shown in Fig. 1. The dihedral angle between the pyridine and pyrazole rings is 64.01 (8)°. The dihedral angle between the mean plane of the pyrazole ring and the plane formed by the atoms C10/O1/O2 is 7.47 (18)°. In the crystal structure, O—H···N hydrogen bonds involving the carboxylic acid O atoms and the 3-chloropyridin-2-yl group N atoms, form one-dimensional chains along [001] (Fig. 2). These chains, are in turn, linked by weak intermolecular C—H···O interactions forming a two-dimensional network perpendicular to the b-axis (Fig. 3).

## Experimental

A mixture of $Zn(OAc)_2.4H_2O$ (21.8 mg, 0.1 mmol), 1-(3-chloropyridin-2-yl)-3- methyl-pyrazole-5-carboxylic acid (23.8 mg, 0.1 mmol) in water (10 ml) was heated at 433 K for 3 d in a sealed Teflon-lined stainless steel vessel (20 ml) under autogenous pressure. After the reaction mixture was slowly cooled to room temperature at a rate of 5 K $h^{-1}$, pale-yellow lamellar single crystals suitable for X-ray diffraction were produced.

## Refinement

Although all H atoms were visible in difference Fourier maps, they were placed in calculated positions, with C-H distances in the range 0.93-0.96Å and an O-H distance of 0.82Å, and included in the final refinement in a riding-model approximation, with $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H) = 1.5U_{eq}(O,C_{methyl})$

## Figures

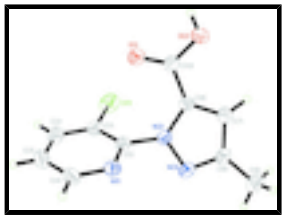


Fig. 1. The molecular structure of (I) showing 30% probability ellipsoids.

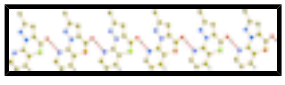


Fig. 2. The one-dimensional chain structure of (I), showing O—H···N hydrogen bonds as red dashed lines.

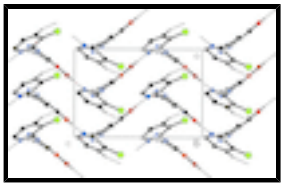


Fig. 3. Part of the crystal structure with hydrogen bonds shown as dashed lines.

### 1-(3-Chloro-2-pyridyl)-3-methyl-1*H*-pyrazole-5-carboxylic acid

*Crystal data*

| | |
|---|---|
| $C_{10}H_8ClN_3O_2$ | $F_{000}$ = 488 |
| $M_r$ = 237.64 | $D_x$ = 1.426 Mg m$^{-3}$ |
| Orthorhombic, $Pca2_1$ | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| Hall symbol: P 2c -2ac | Cell parameters from 2602 reflections |
| $a$ = 8.250 (6) Å | θ = 3.1–27.5º |
| $b$ = 11.232 (8) Å | μ = 0.33 mm$^{-1}$ |
| $c$ = 11.942 (8) Å | $T$ = 296 K |
| $V$ = 1106.6 (13) Å$^3$ | Block, colourless |
| $Z$ = 4 | 0.24 × 0.20 × 0.18 mm |

*Data collection*

| | |
|---|---|
| Bruker SMART APEXII CCD diffractometer | 1943 independent reflections |
| Radiation source: fine-focus sealed tube | 1754 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.032 |
| $T$ = 296 K | $\theta_{max}$ = 25.0º |
| φ and ω scans | $\theta_{min}$ = 1.8º |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h$ = −9→8 |
| $T_{min}$ = 0.582, $T_{max}$ = 1.000 | $k$ = −11→13 |
| 5084 measured reflections | $l$ = −14→14 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)]$ = 0.033 | $w = 1/[\sigma^2(F_o^2) + (0.0254P)^2 + 0.1923P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2)$ = 0.075 | $(\Delta/\sigma)_{max} < 0.001$ |
| $S$ = 1.04 | $\Delta\rho_{max}$ = 0.14 e Å$^{-3}$ |
| 1943 reflections | $\Delta\rho_{min}$ = −0.13 e Å$^{-3}$ |
| 147 parameters | Extinction correction: none |
| 1 restraint | Absolute structure: Flack (1983) 912 Friedel pairs |
| Primary atom site location: structure-invariant direct methods | Flack parameter: 0.03 (7) |

Secondary atom site location: difference Fourier map

*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 $F^2 > \sigma(F^2)$ 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 | 1.19679 (9) | 0.18938 (6) | 0.13597 (6) | 0.0748 (2) |
| O1 | 0.7978 (2) | 0.17726 (13) | 0.1372 (2) | 0.0622 (5) |
| O2 | 0.6983 (2) | 0.34151 (14) | 0.05851 (17) | 0.0664 (5) |
| H2 | 0.6504 | 0.2936 | 0.0186 | 0.100* |
| N1 | 0.9622 (2) | 0.18043 (16) | 0.42451 (15) | 0.0446 (5) |
| N2 | 0.9738 (2) | 0.33015 (15) | 0.29058 (16) | 0.0414 (4) |
| N3 | 1.0231 (2) | 0.42331 (17) | 0.35467 (17) | 0.0490 (5) |
| C1 | 1.1171 (3) | 0.1403 (2) | 0.26170 (19) | 0.0484 (6) |
| C2 | 1.1532 (3) | 0.0288 (2) | 0.3012 (2) | 0.0606 (7) |
| H2A | 1.2178 | −0.0224 | 0.2594 | 0.073* |
| C3 | 1.0928 (3) | −0.0067 (2) | 0.4034 (3) | 0.0625 (7) |
| H3 | 1.1145 | −0.0823 | 0.4314 | 0.075* |
| C4 | 0.9994 (3) | 0.0727 (2) | 0.4629 (2) | 0.0544 (6) |
| H4 | 0.9607 | 0.0501 | 0.5329 | 0.065* |
| C5 | 1.0179 (2) | 0.21361 (19) | 0.32469 (18) | 0.0396 (5) |
| C6 | 0.9573 (3) | 0.5193 (2) | 0.3074 (2) | 0.0502 (6) |
| C7 | 0.8657 (3) | 0.4882 (2) | 0.2137 (2) | 0.0508 (6) |
| H7 | 0.8092 | 0.5395 | 0.1668 | 0.061* |
| C8 | 0.8758 (3) | 0.36675 (19) | 0.20469 (19) | 0.0421 (5) |
| C9 | 0.9834 (4) | 0.6389 (2) | 0.3575 (3) | 0.0786 (9) |
| H9A | 1.0755 | 0.6363 | 0.4066 | 0.118* |
| H9B | 0.8889 | 0.6617 | 0.3992 | 0.118* |
| H9C | 1.0026 | 0.6958 | 0.2991 | 0.118* |
| C10 | 0.7890 (3) | 0.28386 (18) | 0.1310 (2) | 0.0435 (5) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cl1 | 0.0825 (5) | 0.0840 (5) | 0.0578 (4) | 0.0041 (4) | 0.0284 (4) | −0.0126 (4) |
| O1 | 0.0816 (12) | 0.0439 (10) | 0.0612 (10) | −0.0104 (8) | −0.0217 (10) | 0.0019 (10) |
| O2 | 0.0833 (13) | 0.0539 (10) | 0.0618 (12) | −0.0028 (9) | −0.0294 (11) | 0.0010 (9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N1 | 0.0460 (11) | 0.0480 (11) | 0.0399 (11) | −0.0015 (8) | 0.0012 (9) | 0.0004 (8) |
| N2 | 0.0477 (11) | 0.0391 (10) | 0.0376 (10) | −0.0016 (8) | 0.0009 (9) | −0.0041 (8) |
| N3 | 0.0497 (11) | 0.0477 (11) | 0.0496 (11) | −0.0037 (9) | −0.0004 (10) | −0.0108 (9) |
| C1 | 0.0471 (13) | 0.0541 (14) | 0.0441 (13) | 0.0011 (11) | 0.0002 (10) | −0.0101 (11) |
| C2 | 0.0564 (14) | 0.0555 (15) | 0.0701 (17) | 0.0155 (12) | −0.0069 (14) | −0.0158 (13) |
| C3 | 0.0659 (17) | 0.0482 (13) | 0.0734 (18) | 0.0074 (14) | −0.0155 (15) | 0.0052 (13) |
| C4 | 0.0598 (15) | 0.0549 (16) | 0.0484 (13) | −0.0030 (13) | −0.0059 (11) | 0.0096 (11) |
| C5 | 0.0368 (11) | 0.0429 (12) | 0.0391 (12) | −0.0007 (9) | −0.0034 (9) | −0.0053 (9) |
| C6 | 0.0511 (13) | 0.0416 (13) | 0.0578 (15) | −0.0040 (11) | 0.0021 (12) | −0.0096 (11) |
| C7 | 0.0562 (14) | 0.0425 (13) | 0.0539 (13) | 0.0012 (11) | −0.0029 (12) | 0.0017 (11) |
| C8 | 0.0451 (12) | 0.0438 (13) | 0.0373 (11) | −0.0019 (10) | 0.0012 (9) | −0.0007 (10) |
| C9 | 0.088 (2) | 0.0546 (16) | 0.093 (2) | 0.0004 (16) | −0.0138 (19) | −0.0207 (16) |
| C10 | 0.0493 (12) | 0.0425 (12) | 0.0386 (11) | −0.0034 (10) | 0.0030 (11) | 0.0035 (12) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cl1—C1 | 1.729 (3) | C2—H2A | 0.9300 |
| O1—C10 | 1.202 (2) | C3—C4 | 1.376 (4) |
| O2—C10 | 1.314 (3) | C3—H3 | 0.9300 |
| O2—H2 | 0.8200 | C4—H4 | 0.9300 |
| N1—C4 | 1.330 (3) | C6—C7 | 1.394 (4) |
| N1—C5 | 1.331 (3) | C6—C9 | 1.486 (4) |
| N2—N3 | 1.359 (2) | C7—C8 | 1.371 (3) |
| N2—C8 | 1.369 (3) | C7—H7 | 0.9300 |
| N2—C5 | 1.418 (3) | C8—C10 | 1.468 (3) |
| N3—C6 | 1.333 (3) | C9—H9A | 0.9600 |
| C1—C2 | 1.371 (4) | C9—H9B | 0.9600 |
| C1—C5 | 1.383 (3) | C9—H9C | 0.9600 |
| C2—C3 | 1.377 (4) | | |
| C10—O2—H2 | 109.5 | C1—C5—N2 | 123.0 (2) |
| C4—N1—C5 | 118.9 (2) | N3—C6—C7 | 111.0 (2) |
| N3—N2—C8 | 111.56 (16) | N3—C6—C9 | 120.1 (2) |
| N3—N2—C5 | 118.17 (18) | C7—C6—C9 | 128.9 (2) |
| C8—N2—C5 | 130.08 (18) | C8—C7—C6 | 106.2 (2) |
| C6—N3—N2 | 105.21 (18) | C8—C7—H7 | 126.9 |
| C2—C1—C5 | 119.0 (2) | C6—C7—H7 | 126.9 |
| C2—C1—Cl1 | 120.47 (19) | N2—C8—C7 | 106.01 (19) |
| C5—C1—Cl1 | 120.49 (18) | N2—C8—C10 | 123.1 (2) |
| C1—C2—C3 | 119.4 (2) | C7—C8—C10 | 130.4 (2) |
| C1—C2—H2A | 120.3 | C6—C9—H9A | 109.5 |
| C3—C2—H2A | 120.3 | C6—C9—H9B | 109.5 |
| C4—C3—C2 | 118.2 (2) | H9A—C9—H9B | 109.5 |
| C4—C3—H3 | 120.9 | C6—C9—H9C | 109.5 |
| C2—C3—H3 | 120.9 | H9A—C9—H9C | 109.5 |
| N1—C4—C3 | 122.7 (3) | H9B—C9—H9C | 109.5 |
| N1—C4—H4 | 118.6 | O1—C10—O2 | 124.5 (2) |
| C3—C4—H4 | 118.6 | O1—C10—C8 | 124.4 (3) |
| N1—C5—C1 | 121.6 (2) | O2—C10—C8 | 111.10 (19) |
| N1—C5—N2 | 115.29 (19) | | |

| | | | |
|---|---|---|---|
| C8—N2—N3—C6 | −0.9 (2) | C8—N2—C5—C1 | 69.0 (3) |
| C5—N2—N3—C6 | −176.4 (2) | N2—N3—C6—C7 | 0.2 (3) |
| C5—C1—C2—C3 | −1.3 (3) | N2—N3—C6—C9 | 178.8 (2) |
| Cl1—C1—C2—C3 | 177.8 (2) | N3—C6—C7—C8 | 0.6 (3) |
| C1—C2—C3—C4 | −0.8 (4) | C9—C6—C7—C8 | −177.9 (3) |
| C5—N1—C4—C3 | −0.4 (4) | N3—N2—C8—C7 | 1.3 (2) |
| C2—C3—C4—N1 | 1.7 (4) | C5—N2—C8—C7 | 176.0 (2) |
| C4—N1—C5—C1 | −1.9 (3) | N3—N2—C8—C10 | −172.2 (2) |
| C4—N1—C5—N2 | −179.44 (19) | C5—N2—C8—C10 | 2.6 (4) |
| C2—C1—C5—N1 | 2.8 (3) | C6—C7—C8—N2 | −1.1 (2) |
| Cl1—C1—C5—N1 | −176.29 (17) | C6—C7—C8—C10 | 171.7 (2) |
| C2—C1—C5—N2 | −179.9 (2) | N2—C8—C10—O1 | −1.5 (4) |
| Cl1—C1—C5—N2 | 1.0 (3) | C7—C8—C10—O1 | −173.2 (3) |
| N3—N2—C5—N1 | 60.9 (3) | N2—C8—C10—O2 | 177.4 (2) |
| C8—N2—C5—N1 | −113.5 (3) | C7—C8—C10—O2 | 5.7 (4) |
| N3—N2—C5—C1 | −116.5 (2) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2—H2···N1$^{i}$ | 0.82 | 1.93 | 2.755 (3) | 180 |
| C2—H2A···O1$^{ii}$ | 0.93 | 2.36 | 3.258 (4) | 161 |

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

**Fig. 1**

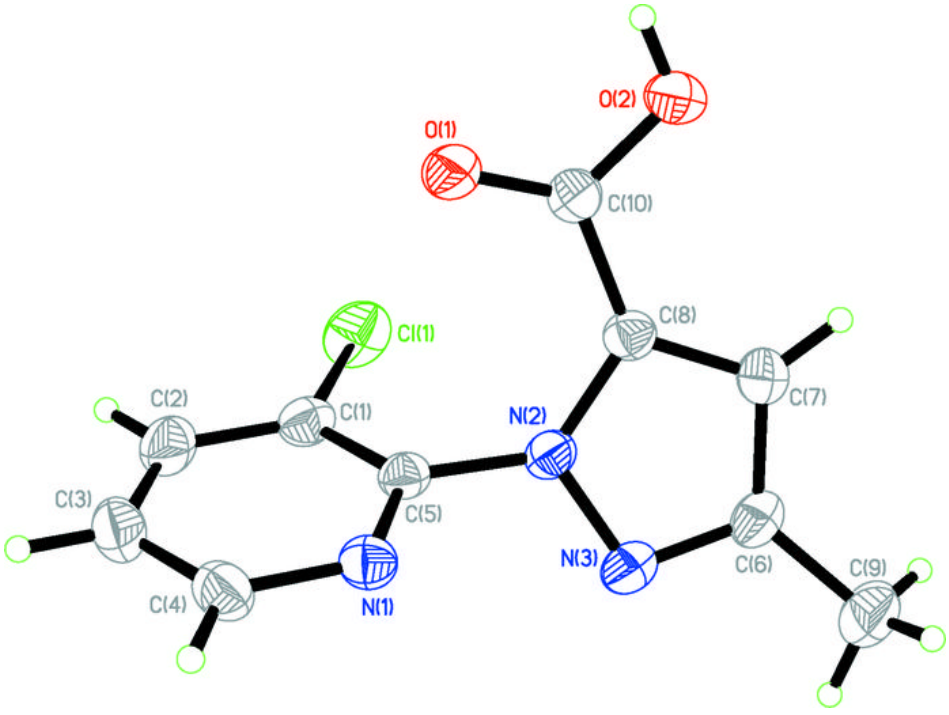


**Fig. 2**

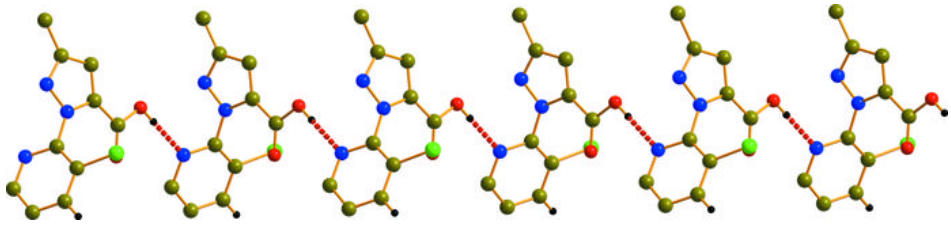


**Fig. 3**