

Ethyl 2-(6-amino-5-cyano-3,4-dimethyl-2H,4H-pyrano[2,3-c]pyrazol-4-yl)acetate

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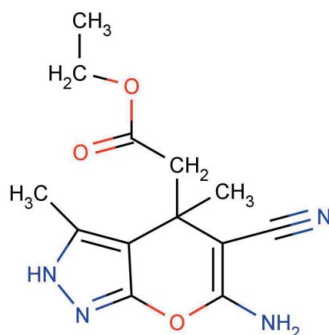
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.041; wR factor = 0.117; data-to-parameter ratio = 12.9.

In the title compound, $\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_3$, the pyrazole ring is planar (r.m.s. deviation = 0.054 Å). The pyran ring is not planar; the mean plane makes a dihedral angle of 1.9 (1)° with the pyrazole ring. In the crystal structure, intermolecular N—H···N and N—H···O interactions lead to a linear chain motif.

Related literature

For biological applications of pyrazole and pyranopyrazole derivatives, see: Wamhoff *et al.* (1993); Velaparthi *et al.* (2008); Magedov *et al.* (2007); Rovnyak *et al.* (1982). For the synthesis, see: Vasuki & Kumaravel (2008).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{16}\text{N}_4\text{O}_3$
 $M_r = 276.30$
 Triclinic, $P\bar{1}$
 $a = 6.961$ (5) Å
 $b = 7.373$ (5) Å
 $c = 14.535$ (5) Å

$\alpha = 86.405$ (5)°
 $\beta = 85.183$ (5)°
 $\gamma = 65.726$ (5)°
 $V = 677.3$ (7) Å³
 $Z = 2$
 Mo $K\alpha$ radiation

$\mu = 0.10$ mm⁻¹
 $T = 293$ K

0.25 × 0.20 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker 2004)
 $T_{\min} = 0.976$, $T_{\max} = 0.981$

12811 measured reflections
 2385 independent reflections
 2130 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.117$
 $S = 1.02$
 2378 reflections

184 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.30$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O2 ⁱ	0.86	2.55	3.274 (2)	142
N2—H2···N1 ⁱⁱ	0.86	2.37	2.956 (2)	126
N3—H3A···N4 ⁱⁱⁱ	0.86	2.19	3.012 (2)	160
N3—H3B···O3 ^{iv}	0.86	2.40	3.192 (2)	154

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

Data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Bruker, 2004); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: PLATON (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2761).

References

- Bruker (2004). APEX2, SAINT and XPREP. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Magedov, I. V., Manpadi, M., Vanslambrouck, S., Steelant, W. F. A., Rozhkova, E., Przhevalskii, N. M., Rogelj, S. & Kornienko, A. (2007). *J. Med. Chem.* **50**, 5183–5192.
- Rovnyak, G. C., Millonig, R. C., Schwartz, J. & Shu, V. (1982). *J. Med. Chem.* **25**, 1482–1488.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Vasuki, G. & Kumaravel, K. (2008). *Tetrahedron Lett.* **49**, 5636–5638.
- Velaparthi, S., Brunsteiner, M., Uddin, R., Wan, B., Franzblau, S. G. & Petukhov, P. A. (2008). *J. Med. Chem.* **51**, 1999–2002.
- Wamhoff, H., Kroth, E. & Strauch, K. (1993). *Synthesis*, **11**, 1129.

supplementary materials

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Ethyl 2-(6-amino-5-cyano-3,4-dimethyl-2*H*,4*H*-pyrano[2,3-*c*]pyrazol-4-yl)acetate

M. Kannan, K. Kumaravel, G. Vasuki and R. Krishna

Comment

Pyrazole, Pyranopyrazoles and its derivatives possess antimicrobial (Velaparthi *et al.*, 2008), anticancer (Magedov *et al.*, 2007) and anti-inflammatory (Rovnyak *et al.*, 1982) properties, which made them to be used as medicines and as biodegradable agrochemicals (Wamhoff *et al.*, 1993). Wide variety of biological importances of these molecules made the quest for their crystal study and accordingly we have synthesized the title compound by multi-component reaction which complies with the principles of green chemistry and reported the crystal structure of the title compound.

The compound was crystallized by slow evaporation technique using ethanol as solvent at room temperature. The title compound, (I) was centrosymmetric and it has triclinic crystal system with the space group of *P*-1. The pyrazole groups are essentially planar, with a mean deviation of 0.0542 Å from the least square plane defined by the five atoms (N1 to C1). The pyran ring deviates significantly from the plane and it has dihedral angle of 1.93 (0.06)° with pyrazole ring. The ethyl acetate group has dihedral angle of 49.99 (0.07)° with pyran ring to which it is attached (Fig. 1). The intermolecular hydrogen bond was formed between N2...N1, N3...N4, N2—H...O2 and N3—H...O3 with distance of 2.956 (2), 3.012 (2), 3.274 (2) and 3.192 (2) Å respectively (Table.1). These intermolecular interactions help in the formation three-dimensional network and crystal packing (Fig. 2) of (I).

Experimental

The titled compound was prepared by the successive addition of malononitrile (0.132 g, 2 mmol) and piperidine (5 mol%) to a stirred aqueous mixture of hydrazine hydrate 96% 1 (0.107 g, 2 mmol) and ethyl acetoacetate 2 (0.520 g, 4 mmol) at room temperature under an open atmosphere with vigorous stirring for 5–10 min. The precipitated solid was filtered, washed with water and then with a mixture of ethyl acetate/hexane (20:80) (Vasuki & Kumaravel, 2008). The product obtained was pure by TLC and ¹H NMR spectroscopy. However, the products were further purified by recrystallization from ethanol. Analysis calculated for ethyl 2-(6-amino-5-cyano-3,4-dimethyl-2,4-dihydropyrano[2,3-*c*]pyrazol-4-yl) acetate showed that it has C₁₃, H₁₆, N₄, O₃.

Refinement

The non-hydrogen atoms were refined anisotropically whereas hydrogen atoms were refined isotropically. The H atoms were geometrically placed (N—H = 0.86 Å, and C—H = 0.93–0.97 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5 U_{\text{eq}}$ (parent atom).

Figures

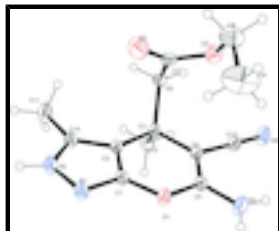


Fig. 1. : The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 30% probability level.

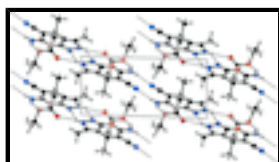


Fig. 2. : The crystal packing of (I), showing intermolecular hydrogen bonding interactions as dashed lines.

Ethyl 2-(6-amino-5-cyano-3,4-dimethyl-2*H*,4*H*- pyrano[2,3-*c*]pyrazol-4-yl)acetate

Crystal data

$C_{13}H_{16}N_4O_3$

$M_r = 276.30$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 6.961\ (5)\ \text{\AA}$

$b = 7.373\ (5)\ \text{\AA}$

$c = 14.535\ (5)\ \text{\AA}$

$\alpha = 86.405\ (5)^\circ$

$\beta = 85.183\ (5)^\circ$

$\gamma = 65.726\ (5)^\circ$

$V = 677.3\ (7)\ \text{\AA}^3$

$Z = 2$

$F(000) = 292$

$D_x = 1.355\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71069\ \text{\AA}$

Cell parameters from 7682 reflections

$\theta = 2.8\text{--}32.8^\circ$

$\mu = 0.10\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colourless

$0.25 \times 0.20 \times 0.20\ \text{mm}$

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: $0\ \text{pixels mm}^{-1}$

ω and ϕ scan

Absorption correction: multi-scan
(SADABS; Bruker 2004)

$T_{\min} = 0.976$, $T_{\max} = 0.981$

12811 measured reflections

2385 independent reflections

2130 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -8 \rightarrow 8$

$k = -8 \rightarrow 8$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct
methods

Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.041$$

$$wR(F^2) = 0.117$$

$$S = 1.02$$

2378 reflections

184 parameters

0 restraints

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0655P)^2 + 0.2561P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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.

Some "bad" reflections were omitted in the refinement.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.4375 (2)	0.8266 (2)	0.84125 (10)	0.0288 (3)
C2	0.3125 (2)	0.7231 (2)	0.86328 (9)	0.0271 (3)
C3	0.2551 (2)	0.6151 (2)	0.79351 (9)	0.0271 (3)
C4	0.3682 (2)	0.6404 (2)	0.70213 (9)	0.0282 (3)
C5	0.4908 (2)	0.7439 (2)	0.68793 (10)	0.0306 (3)
C6	0.0126 (2)	0.7009 (2)	0.78369 (10)	0.0329 (3)
H6A	-0.0164	0.6276	0.7375	0.040*
H6B	-0.0563	0.6818	0.8420	0.040*
C7	-0.0780 (2)	0.9167 (2)	0.75667 (11)	0.0378 (4)
C8	-0.1525 (3)	1.1488 (3)	0.62848 (17)	0.0654 (6)
H8A	-0.2528	1.2402	0.6724	0.078*
H8B	-0.2217	1.1636	0.5715	0.078*
C9	0.0317 (5)	1.1990 (4)	0.6104 (3)	0.1088 (12)
H9A	0.0887	1.2023	0.6679	0.163*
H9B	-0.0109	1.3271	0.5794	0.163*
H9C	0.1375	1.1003	0.5722	0.163*
C10	0.2672 (2)	0.7477 (2)	0.95731 (10)	0.0320 (3)
C11	0.1408 (3)	0.6754 (3)	1.02539 (11)	0.0487 (5)
H11A	0.2177	0.5356	1.0380	0.073*
H11B	0.0091	0.6978	1.0006	0.073*
H11C	0.1140	0.7461	1.0816	0.073*

supplementary materials

C12	0.3282 (3)	0.3931 (2)	0.82003 (11)	0.0385 (4)
H12A	0.4780	0.3351	0.8261	0.058*
H12B	0.2951	0.3270	0.7729	0.058*
H12C	0.2574	0.3782	0.8777	0.058*
C13	0.3419 (2)	0.5481 (2)	0.62484 (10)	0.0354 (4)
N1	0.4738 (2)	0.9108 (2)	0.91081 (8)	0.0351 (3)
N2	0.3649 (2)	0.8596 (2)	0.98199 (8)	0.0357 (3)
H2	0.3589	0.8954	1.0377	0.043*
N3	0.5923 (2)	0.7662 (2)	0.60839 (9)	0.0474 (4)
H3A	0.5831	0.7114	0.5594	0.057*
H3B	0.6667	0.8352	0.6064	0.057*
N4	0.3189 (3)	0.4715 (3)	0.56322 (10)	0.0555 (4)
O1	0.52556 (17)	0.84545 (17)	0.75515 (7)	0.0367 (3)
O2	-0.1338 (2)	1.0482 (2)	0.81014 (10)	0.0659 (4)
O3	-0.08990 (18)	0.94621 (17)	0.66504 (8)	0.0450 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0306 (7)	0.0354 (7)	0.0243 (7)	-0.0169 (6)	-0.0013 (5)	-0.0047 (6)
C2	0.0271 (7)	0.0322 (7)	0.0246 (7)	-0.0142 (6)	-0.0018 (5)	-0.0038 (5)
C3	0.0277 (7)	0.0322 (7)	0.0250 (7)	-0.0153 (6)	-0.0012 (5)	-0.0050 (5)
C4	0.0269 (7)	0.0353 (7)	0.0253 (7)	-0.0148 (6)	-0.0007 (5)	-0.0071 (6)
C5	0.0307 (7)	0.0399 (8)	0.0245 (7)	-0.0172 (6)	-0.0006 (6)	-0.0069 (6)
C6	0.0291 (7)	0.0450 (8)	0.0312 (8)	-0.0213 (6)	0.0005 (6)	-0.0068 (6)
C7	0.0250 (7)	0.0454 (9)	0.0434 (9)	-0.0128 (6)	-0.0036 (6)	-0.0124 (7)
C8	0.0592 (12)	0.0478 (11)	0.0810 (15)	-0.0144 (9)	-0.0116 (11)	0.0124 (10)
C9	0.096 (2)	0.0740 (17)	0.171 (3)	-0.0526 (16)	-0.029 (2)	0.0415 (19)
C10	0.0376 (8)	0.0365 (8)	0.0267 (7)	-0.0196 (6)	-0.0016 (6)	-0.0048 (6)
C11	0.0692 (12)	0.0637 (11)	0.0298 (8)	-0.0450 (10)	0.0083 (8)	-0.0090 (8)
C12	0.0481 (9)	0.0344 (8)	0.0364 (8)	-0.0197 (7)	-0.0038 (7)	-0.0028 (6)
C13	0.0362 (8)	0.0488 (9)	0.0289 (8)	-0.0255 (7)	0.0042 (6)	-0.0088 (7)
N1	0.0430 (7)	0.0457 (7)	0.0273 (6)	-0.0284 (6)	-0.0011 (5)	-0.0067 (5)
N2	0.0487 (8)	0.0459 (7)	0.0224 (6)	-0.0286 (6)	-0.0015 (5)	-0.0069 (5)
N3	0.0591 (9)	0.0738 (10)	0.0300 (7)	-0.0484 (8)	0.0114 (6)	-0.0162 (7)
N4	0.0675 (10)	0.0859 (12)	0.0357 (8)	-0.0534 (9)	0.0097 (7)	-0.0243 (8)
O1	0.0446 (6)	0.0537 (7)	0.0266 (6)	-0.0350 (5)	0.0047 (4)	-0.0106 (5)
O2	0.0652 (9)	0.0518 (8)	0.0677 (9)	-0.0048 (7)	-0.0160 (7)	-0.0270 (7)
O3	0.0440 (7)	0.0432 (6)	0.0457 (7)	-0.0163 (5)	-0.0008 (5)	-0.0005 (5)

Geometric parameters (\AA , $^\circ$)

C1—N1	1.3125 (19)	C8—H8A	0.9700
C1—O1	1.3714 (18)	C8—H8B	0.9700
C1—C2	1.383 (2)	C9—H9A	0.9600
C2—C10	1.383 (2)	C9—H9B	0.9600
C2—C3	1.5006 (19)	C9—H9C	0.9600
C3—C4	1.527 (2)	C10—N2	1.346 (2)
C3—C12	1.535 (2)	C10—C11	1.487 (2)

C3—C6	1.556 (2)	C11—H11A	0.9600
C4—C5	1.356 (2)	C11—H11B	0.9600
C4—C13	1.411 (2)	C11—H11C	0.9600
C5—N3	1.341 (2)	C12—H12A	0.9600
C5—O1	1.3616 (17)	C12—H12B	0.9600
C6—C7	1.490 (2)	C12—H12C	0.9600
C6—H6A	0.9700	C13—N4	1.144 (2)
C6—H6B	0.9700	N1—N2	1.3572 (18)
C7—O2	1.195 (2)	N2—H2	0.8600
C7—O3	1.340 (2)	N3—H3A	0.8600
C8—O3	1.452 (2)	N3—H3B	0.8600
C8—C9	1.474 (4)		
N1—C1—O1	118.81 (13)	H8A—C8—H8B	108.0
N1—C1—C2	115.28 (13)	C8—C9—H9A	109.5
O1—C1—C2	125.90 (13)	C8—C9—H9B	109.5
C1—C2—C10	103.21 (13)	H9A—C9—H9B	109.5
C1—C2—C3	123.21 (13)	C8—C9—H9C	109.5
C10—C2—C3	133.58 (13)	H9A—C9—H9C	109.5
C2—C3—C4	105.90 (12)	H9B—C9—H9C	109.5
C2—C3—C12	111.39 (12)	N2—C10—C2	106.01 (13)
C4—C3—C12	109.91 (12)	N2—C10—C11	122.04 (14)
C2—C3—C6	112.12 (11)	C2—C10—C11	131.95 (14)
C4—C3—C6	110.22 (12)	C10—C11—H11A	109.5
C12—C3—C6	107.33 (12)	C10—C11—H11B	109.5
C5—C4—C13	116.78 (13)	H11A—C11—H11B	109.5
C5—C4—C3	126.29 (13)	C10—C11—H11C	109.5
C13—C4—C3	116.93 (13)	H11A—C11—H11C	109.5
N3—C5—C4	126.98 (14)	H11B—C11—H11C	109.5
N3—C5—O1	109.58 (13)	C3—C12—H12A	109.5
C4—C5—O1	123.44 (13)	C3—C12—H12B	109.5
C7—C6—C3	112.62 (12)	H12A—C12—H12B	109.5
C7—C6—H6A	109.1	C3—C12—H12C	109.5
C3—C6—H6A	109.1	H12A—C12—H12C	109.5
C7—C6—H6B	109.1	H12B—C12—H12C	109.5
C3—C6—H6B	109.1	N4—C13—C4	178.79 (17)
H6A—C6—H6B	107.8	C1—N1—N2	101.70 (12)
O2—C7—O3	123.82 (17)	C10—N2—N1	113.80 (12)
O2—C7—C6	124.23 (16)	C10—N2—H2	123.1
O3—C7—C6	111.94 (13)	N1—N2—H2	123.1
O3—C8—C9	111.08 (18)	C5—N3—H3A	120.0
O3—C8—H8A	109.4	C5—N3—H3B	120.0
C9—C8—H8A	109.4	H3A—N3—H3B	120.0
O3—C8—H8B	109.4	C5—O1—C1	115.14 (12)
C9—C8—H8B	109.4	C7—O3—C8	117.56 (15)
N1—C1—C2—C10	0.13 (17)	C12—C3—C6—C7	-179.24 (12)
O1—C1—C2—C10	179.38 (13)	C3—C6—C7—O2	-85.9 (2)
N1—C1—C2—C3	-179.36 (12)	C3—C6—C7—O3	94.18 (15)
O1—C1—C2—C3	-0.1 (2)	C1—C2—C10—N2	0.13 (16)

supplementary materials

C1—C2—C3—C4	2.14 (18)	C3—C2—C10—N2	179.54 (14)
C10—C2—C3—C4	-177.17 (15)	C1—C2—C10—C11	-179.84 (17)
C1—C2—C3—C12	121.60 (15)	C3—C2—C10—C11	-0.4 (3)
C10—C2—C3—C12	-57.7 (2)	C5—C4—C13—N4	169 (9)
C1—C2—C3—C6	-118.10 (15)	C3—C4—C13—N4	-11 (9)
C10—C2—C3—C6	62.6 (2)	O1—C1—N1—N2	-179.63 (12)
C2—C3—C4—C5	-1.37 (19)	C2—C1—N1—N2	-0.32 (17)
C12—C3—C4—C5	-121.80 (16)	C2—C10—N2—N1	-0.35 (17)
C6—C3—C4—C5	120.10 (16)	C11—C10—N2—N1	179.63 (15)
C2—C3—C4—C13	178.97 (12)	C1—N1—N2—C10	0.41 (17)
C12—C3—C4—C13	58.54 (17)	N3—C5—O1—C1	-177.10 (12)
C6—C3—C4—C13	-59.56 (17)	C4—C5—O1—C1	3.8 (2)
C13—C4—C5—N3	-0.9 (2)	N1—C1—O1—C5	176.23 (12)
C3—C4—C5—N3	179.41 (14)	C2—C1—O1—C5	-3.0 (2)
C13—C4—C5—O1	178.03 (13)	O2—C7—O3—C8	7.0 (2)
C3—C4—C5—O1	-1.6 (2)	C6—C7—O3—C8	-173.07 (14)
C2—C3—C6—C7	58.13 (16)	C9—C8—O3—C7	87.2 (3)
C4—C3—C6—C7	-59.57 (16)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2 \cdots O2 ⁱ	0.86	2.55	3.274 (2)	142
N2—H2 \cdots N1 ⁱⁱ	0.86	2.37	2.956 (2)	126
N3—H3A \cdots N4 ⁱⁱⁱ	0.86	2.19	3.012 (2)	160
N3—H3B \cdots O3 ^{iv}	0.86	2.40	3.192 (2)	154

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

Fig. 1

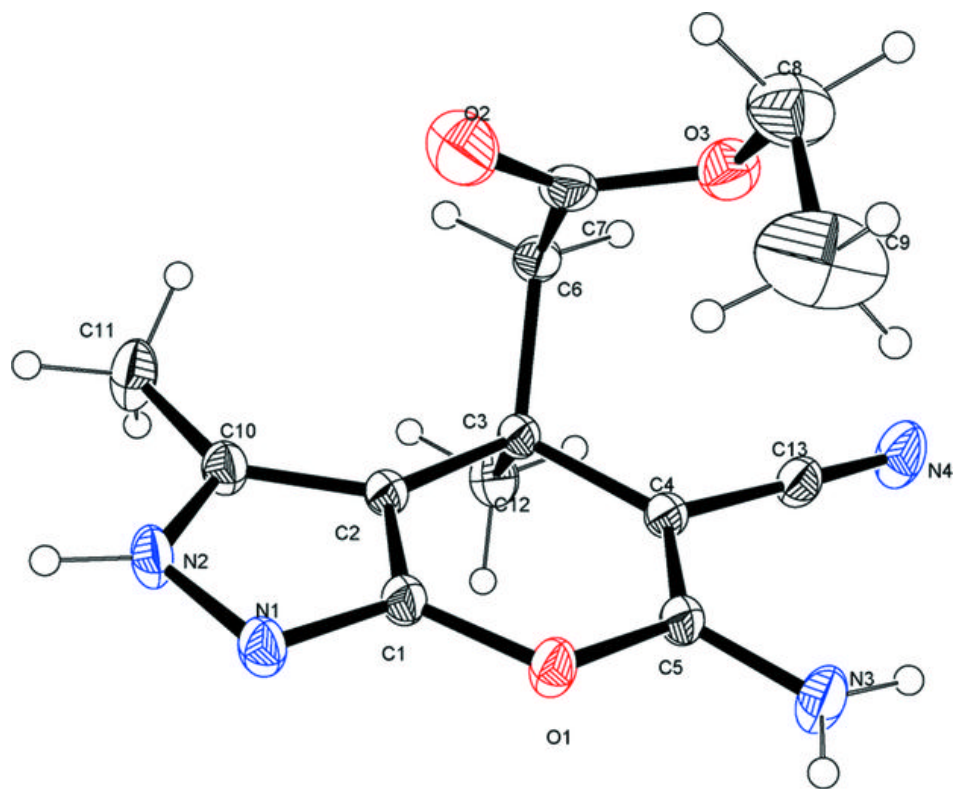


Fig. 2

