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3-Amino-5-methyl-5-(4-pyridyl)-hydantoin

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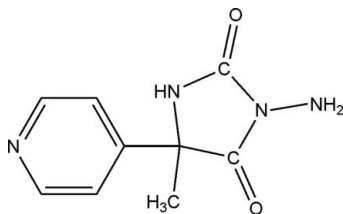
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 Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.046; wR factor = 0.127; data-to-parameter ratio = 19.2.

The title compound, 3-amino-5-methyl-5-(4-pyridyl)imidazolidine-2,4-dione, $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_2$, was obtained by reaction of 5-methyl-5-(4-pyridyl)hydantoin with hydrazine. It crystallizes as a racemate in the tetragonal space group $I4_1/a$ with one molecule in the asymmetric unit. The dihedral angle between the pyridine ring and the five-membered hydantoin ring is 47.99 (3)°. In the crystal structure, molecules are joined in a three-dimensional hydrogen-bonded network by $\text{N}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ links.

Related literature

For the biological activity of hydantoin derivatives and their metal complexes, see: Rajic *et al.* (2006); Bazil *et al.* (1998); Bakalova *et al.* (2005, 2008, 2009). For crystal structures of other 3-amino substituted hydantoins and their metal complexes, see: Shivachev *et al.* (2005); Bakalova *et al.* (2007). For the synthesis of 5-methyl-5-(4-pyridyl)-hydantoin, see: Chu & Teague (1958). For the preparation of 3-amino-hydantoins, see: Davidson (1964).



Experimental

Crystal data

 $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_2$
 $M_r = 206.21$

Tetragonal, $I4_1/a$
 $a = 12.8282$ (5) Å
 $c = 22.9016$ (17) Å
 $V = 3768.8$ (3) Å³
 $Z = 16$

Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 100$ K
 $0.50 \times 0.50 \times 0.50$ mm

Data collection

Bruker X8 APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.948$, $T_{\max} = 0.948$

51879 measured reflections
 2765 independent reflections
 2179 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.076$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.127$
 $S = 1.03$
 2765 reflections
 144 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.56$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.44$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H2}\cdots\text{N4}^{\text{i}}$	0.88	2.69	3.526	159
$\text{N2}-\text{H2}\cdots\text{O2}^{\text{i}}$	0.88	2.26	2.9184 (15)	131
$\text{N4}-\text{H4A}\cdots\text{O1}^{\text{ii}}$	0.977 (19)	2.139 (19)	3.0676 (16)	158.07
$\text{N4}-\text{H4B}\cdots\text{O1}^{\text{iii}}$	0.96 (2)	2.17 (2)	3.1003 (16)	162.23

Symmetry codes: (i) $-y + \frac{5}{4}, x - \frac{1}{4}, z - \frac{1}{4}$; (ii) $y - \frac{1}{4}, -x + \frac{5}{4}, -z + \frac{1}{4}$; (iii) $-y + \frac{5}{4}, x + \frac{1}{4}, -z + \frac{1}{4}$

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); 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); software used to prepare material for publication: SHELXTL.

The authors are indebted to Professor V. Arion of the Institute of Inorganic Chemistry of the University of Vienna for discussions about the X-ray data.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2752).

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supplementary materials

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3-Amino-5-methyl-5-(4-pyridyl)hydantoin

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Comment

Some hydantoin derivatives are biologically active molecules with anticonvulsive, antiarrhythmic, antimicrobial, antiviral or cytostatic activity (Rajic *et al.*, 2006; Bazil *et al.*, 1998). 5-Methyl-5-(4-pyridyl)hydantoin was synthesized by Chu (Chu *et al.* 1958). This compound was used as starting material for preparation of new 3-amino-5-methyl-5-(4-pyridyl)hydantoin (AMPH). These hydantoin derivatives were utilized as carrier ligands for synthesis of new platinum and palladium complexes with potential cytotoxic activity. (Bakalova *et al.*, 2008, 2009). In the recent work we synthesized AMPH (I) by the method of Davidson (Davidson, 1964) with some modifications. The new compound was characterized by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy and molar conductivity. Suitable crystals of AMPH for X-ray diffraction analysis have been isolated and its structure was determined. The result of X-ray diffraction study of 3-amino-5-methyl-5-(4-pyridyl)hydantoin is shown in Fig. 1. The racemic compound crystallizes in the tetragonal space group $I4_1/a$ with one molecule in the asymmetric unit. The presence of the sp^3 -hybridized chiral carbon atom C1 is responsible for the dihedral angle between the pyridine ring and five-membered C_3N_2 ring of *ca* 48° . The sum of the angles around N4 is clearly smaller than 360° (327.0°), indicating its trigonal-pyramidal configuration. The lone-pair region at N4 is directed towards adjacent atom O1. The secondary amine nitrogen N2 acts as a proton donor in an intermolecular bifurcated hydrogen bonding interactions with the nitrogen atom N4 and oxygen atom O2 of the neighbouring molecule of AMPH (Fig. 2) The hydrazinic atom N4 is involved in two intermolecular H bonds with the atoms O1ⁱⁱ and O1ⁱⁱⁱ of the two different neighbouring molecules (Table 1).

Experimental

3-Amino-5-methyl-5-(4-pyridyl)hydantoin was synthesized by dissolving 5-methyl-5(4-pyridyl)hydantoin (1.91 g, 10 mmol) in 98% $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (5 cm^3) and refluxing the solution for 2 h. The reaction mixture was cooled to room temperature and water (15 cm^3) was added. The solution was placed in refrigerator for 24 h. The white product was filtered off, recrystallized from ethanol and dried at 373 K for 5 h. The purity was checked by TLC. The substance is soluble in DMSO and weakly soluble in water and ethanol. Yield: 1.26 g, 61%, m.p. = 523.2–524.7 K. Crystals, suitable for X-ray data collection were grown by slow evaporation from ethanol solution at 277 K. Analysis calculated for $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_2$: C 52.42, H 4.89, N 27.17%. Found: C 52.23, H 4.46, N 26.83%. $\lambda_{\text{M}} = 0.979\text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$; IR(pellets KBr)/ cm^{-1} : 3314.0, 3276.0, 1766.9, 1713.0, 1597.2 and 1411.1. ^1H NMR (250 MHz; DMSO- d_6): 8.95 (1H, s, N(1)—H), 8.59 (2H, d, $J=7$ Hz, H-2, H-6), 7.50 (2H, d, $J=7$ Hz, H-3, H-5), 4.80 (2H, s, NH₂), 1.66 (3H, s, CH₃). ^{13}C NMR (62.5 MHz; DMSO- d_6): 172.7 (C=O-4'), 155.5 (C=O-2'), 150.0 (C-2,C-6), 148.4 (C-4), 120.6 (C-3, C-5), 60.8 (C-5'), 24.7 (CH₃).

Refinement

H atoms were placed at calculated positions [$\text{N—H} = 0.88\text{ \AA}$, $\text{C—H} = 0.95$ and 0.98 \AA] and refined as riding atoms in the subsequent least squares model refinements, except two hydrogen atoms at N4 which were localized from difference map.

supplementary materials

The isotropic thermal parameters of hydrogen atoms in the positions of which were calculated were estimated to be 1.2 or 1.5 times the values of the equivalent isotropic thermal parameters of the atoms to which H atoms were bonded.

Figures

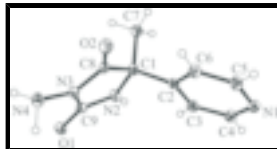


Fig. 1. View of the molecule of AMPH with atom labeling scheme; the thermal ellipsoids are drawn at 50% probability level.

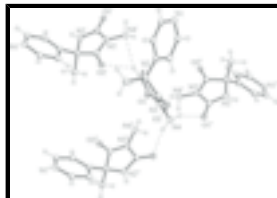


Fig. 2. Fragment of the crystal structure of AMPH showing the intermolecular hydrogen bonding interactions. [Symmetry codes: (i) $-y + 1.25, x - 0.25, z - 0.25$; (ii) $y - 0.25, -x + 1.25, -z + 0.25$; (iii) $-y + 1.25, x + 0.25, -z + 0.25$].

3-amino-5-methyl-5-(4-pyridyl)imidazolidene-2,4-dione

Crystal data

$C_9H_{10}N_4O_2$

$M_r = 206.21$

Tetragonal, $I4_1/a$

Hall symbol: $-I\ 4ad$

$a = 12.8282\ (5)\ \text{\AA}$

$b = 12.8282\ (5)\ \text{\AA}$

$c = 22.9016\ (17)\ \text{\AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 90^\circ$

$V = 3768.8\ (3)\ \text{\AA}^3$

$Z = 16$

$F_{000} = 1728$

$D_x = 1.454\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 847 reflections

$\theta = 2.9\text{--}29.5^\circ$

$\mu = 0.11\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Block, colourless

$0.50 \times 0.50 \times 0.50\ \text{mm}$

Data collection

Bruker X8 APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100\ \text{K}$

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2005)

$T_{\min} = 0.948, T_{\max} = 0.948$

51879 measured reflections

2765 independent reflections

2179 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.076$

$\theta_{\max} = 30.1^\circ$

$\theta_{\min} = 2.9^\circ$

$h = -18 \rightarrow 18$

$k = -18 \rightarrow 18$

$l = -32 \rightarrow 32$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.127$	$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 3.9566P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
2765 reflections	$(\Delta/\sigma)_{\max} < 0.001$
144 parameters	$\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.44 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.59104 (8)	0.59567 (7)	0.06315 (4)	0.0171 (2)
O2	0.68145 (8)	0.42948 (8)	0.23252 (4)	0.0203 (2)
N1	0.58287 (9)	0.06249 (9)	0.13055 (5)	0.0176 (2)
N2	0.67304 (9)	0.43740 (9)	0.07949 (5)	0.0150 (2)
H2	0.6820	0.4172	0.0431	0.018*
N3	0.62479 (8)	0.53105 (8)	0.15592 (5)	0.0128 (2)
N4	0.57993 (10)	0.61113 (9)	0.18907 (5)	0.0181 (2)
H4A	0.5062 (15)	0.6163 (15)	0.1787 (8)	0.027 (5)*
H4B	0.6100 (16)	0.6781 (17)	0.1806 (9)	0.036 (5)*
C1	0.70691 (10)	0.37686 (10)	0.12997 (5)	0.0136 (3)
C2	0.65758 (10)	0.26869 (10)	0.13127 (5)	0.0131 (2)
C3	0.63039 (11)	0.21921 (10)	0.07925 (6)	0.0165 (3)
H3	0.6365	0.2547	0.0430	0.020*
C4	0.59419 (11)	0.11717 (11)	0.08121 (6)	0.0178 (3)
H4	0.5764	0.0843	0.0454	0.021*
C5	0.60863 (11)	0.11133 (11)	0.18034 (6)	0.0179 (3)
H5	0.6008	0.0742	0.2160	0.021*
C6	0.64606 (11)	0.21278 (10)	0.18292 (6)	0.0165 (3)

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H6	0.6635	0.2435	0.2194	0.020*
C7	0.82617 (11)	0.36654 (11)	0.13212 (7)	0.0201 (3)
H7A	0.8578	0.4360	0.1312	0.030*
H7B	0.8502	0.3262	0.0984	0.030*
H7C	0.8466	0.3308	0.1682	0.030*
C8	0.67014 (10)	0.44623 (10)	0.18059 (6)	0.0139 (3)
C9	0.62667 (10)	0.52740 (10)	0.09462 (5)	0.0132 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0197 (5)	0.0162 (5)	0.0154 (5)	0.0016 (4)	-0.0004 (3)	0.0034 (3)
O2	0.0299 (6)	0.0178 (5)	0.0131 (5)	0.0007 (4)	-0.0040 (4)	0.0002 (4)
N1	0.0152 (5)	0.0153 (5)	0.0223 (6)	-0.0003 (4)	0.0004 (4)	0.0004 (4)
N2	0.0195 (5)	0.0145 (5)	0.0109 (5)	0.0020 (4)	0.0019 (4)	0.0013 (4)
N3	0.0136 (5)	0.0132 (5)	0.0117 (5)	0.0002 (4)	0.0011 (4)	-0.0005 (4)
N4	0.0194 (6)	0.0169 (6)	0.0180 (6)	0.0016 (4)	0.0023 (4)	-0.0030 (4)
C1	0.0153 (6)	0.0130 (6)	0.0126 (6)	0.0006 (4)	0.0000 (4)	0.0010 (4)
C2	0.0114 (5)	0.0127 (6)	0.0151 (6)	0.0014 (4)	0.0006 (4)	0.0005 (4)
C3	0.0177 (6)	0.0172 (6)	0.0146 (6)	0.0010 (5)	-0.0012 (5)	0.0008 (5)
C4	0.0178 (6)	0.0172 (6)	0.0183 (6)	0.0000 (5)	-0.0019 (5)	-0.0027 (5)
C5	0.0193 (6)	0.0162 (6)	0.0182 (6)	-0.0008 (5)	0.0013 (5)	0.0031 (5)
C6	0.0189 (6)	0.0160 (6)	0.0145 (6)	-0.0008 (5)	0.0005 (5)	0.0006 (5)
C7	0.0140 (6)	0.0175 (6)	0.0286 (7)	-0.0002 (5)	0.0006 (5)	0.0027 (5)
C8	0.0140 (6)	0.0134 (6)	0.0143 (6)	-0.0025 (4)	-0.0013 (4)	-0.0001 (4)
C9	0.0120 (6)	0.0151 (6)	0.0126 (6)	-0.0019 (5)	0.0011 (4)	0.0004 (4)

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

O1—C9	1.2229 (16)	C1—C8	1.5355 (18)
O2—C8	1.2174 (16)	C1—C7	1.5364 (19)
N1—C4	1.3378 (18)	C2—C6	1.3913 (18)
N1—C5	1.3425 (18)	C2—C3	1.3942 (18)
N2—C9	1.3442 (17)	C3—C4	1.3897 (19)
N2—C1	1.4589 (16)	C3—H3	0.9500
N2—H2	0.8800	C4—H4	0.9500
N3—C8	1.3571 (17)	C5—C6	1.3884 (19)
N3—N4	1.4010 (16)	C5—H5	0.9500
N3—C9	1.4047 (17)	C6—H6	0.9500
N4—H4A	0.978 (19)	C7—H7A	0.9800
N4—H4B	0.96 (2)	C7—H7B	0.9800
C1—C2	1.5254 (18)	C7—H7C	0.9800
C4—N1—C5	116.49 (12)	N1—C4—C3	123.89 (13)
C9—N2—C1	112.63 (11)	N1—C4—H4	118.1
C9—N2—H2	123.7	C3—C4—H4	118.1
C1—N2—H2	123.7	N1—C5—C6	123.97 (13)
C8—N3—N4	122.57 (11)	N1—C5—H5	118.0
C8—N3—C9	112.46 (10)	C6—C5—H5	118.0

N4—N3—C9	124.96 (11)	C5—C6—C2	118.94 (12)
N3—N4—H4A	108.4 (11)	C5—C6—H6	120.5
N3—N4—H4B	112.4 (12)	C2—C6—H6	120.5
H4A—N4—H4B	106.2 (17)	C1—C7—H7A	109.5
N2—C1—C2	112.09 (10)	C1—C7—H7B	109.5
N2—C1—C8	101.43 (10)	H7A—C7—H7B	109.5
C2—C1—C8	112.65 (10)	C1—C7—H7C	109.5
N2—C1—C7	111.58 (11)	H7A—C7—H7C	109.5
C2—C1—C7	109.52 (11)	H7B—C7—H7C	109.5
C8—C1—C7	109.37 (11)	O2—C8—N3	126.83 (12)
C6—C2—C3	117.73 (12)	O2—C8—C1	126.77 (12)
C6—C2—C1	121.97 (11)	N3—C8—C1	106.38 (11)
C3—C2—C1	120.09 (11)	O1—C9—N2	128.95 (12)
C4—C3—C2	119.00 (12)	O1—C9—N3	123.97 (12)
C4—C3—H3	120.5	N2—C9—N3	107.08 (11)
C2—C3—H3	120.5		
C9—N2—C1—C2	121.59 (12)	N4—N3—C8—O2	-2.7 (2)
C9—N2—C1—C8	1.19 (14)	C9—N3—C8—O2	178.47 (13)
C9—N2—C1—C7	-115.16 (12)	N4—N3—C8—C1	178.74 (11)
N2—C1—C2—C6	-155.89 (12)	C9—N3—C8—C1	-0.11 (14)
C8—C1—C2—C6	-42.24 (17)	N2—C1—C8—O2	-179.19 (13)
C7—C1—C2—C6	79.71 (15)	C2—C1—C8—O2	60.81 (17)
N2—C1—C2—C3	29.50 (16)	C7—C1—C8—O2	-61.23 (17)
C8—C1—C2—C3	143.15 (12)	N2—C1—C8—N3	-0.61 (13)
C7—C1—C2—C3	-94.90 (14)	C2—C1—C8—N3	-120.62 (11)
C6—C2—C3—C4	-0.49 (19)	C7—C1—C8—N3	117.35 (12)
C1—C2—C3—C4	174.35 (12)	C1—N2—C9—O1	179.01 (13)
C5—N1—C4—C3	0.0 (2)	C1—N2—C9—N3	-1.30 (14)
C2—C3—C4—N1	0.4 (2)	C8—N3—C9—O1	-179.43 (12)
C4—N1—C5—C6	-0.4 (2)	N4—N3—C9—O1	1.8 (2)
N1—C5—C6—C2	0.4 (2)	C8—N3—C9—N2	0.86 (14)
C3—C2—C6—C5	0.1 (2)	N4—N3—C9—N2	-177.95 (11)
C1—C2—C6—C5	-174.61 (12)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots O2 ⁱ	0.88	2.26	2.9184 (15)	131
N2—H2 \cdots N4 ⁱ	0.88	2.69	3.526	159
N4—H4A \cdots O1 ⁱⁱ	0.977 (19)	2.139 (19)	3.0676 (16)	158.07
N4—H4B \cdots O1 ⁱⁱⁱ	0.96 (2)	2.17 (2)	3.1003 (16)	162.23

Symmetry codes: (i) $-y+5/4, x-1/4, z-1/4$; (ii) $y-1/4, -x+5/4, -z+1/4$; (iii) $-y+5/4, x+1/4, -z+1/4$.

Fig. 1

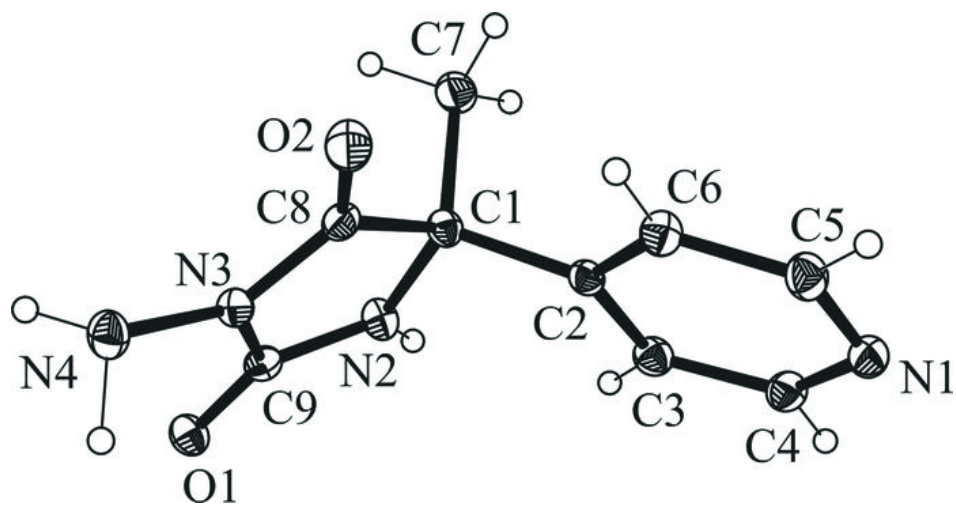


Fig. 2

