Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Methyl 6-amino-5-cyano-4-(4-fluorophenyl)-2-methylpyridine-3-carboxylate

Qian Wang,[a]* Dianxiang Zhou,[b] Chunmei Li,[b] Qingqing Shao[b] and Shujiang Tu[b]

[a]Xuzhou Medical College, Jiangsu 221004, People's Republic of China, and [b]School of Chemistry and Chemical Engineering, Xuzhou Normal University, Xuzhou 221116, People's Republic of China
Correspondence e-mail: laotu2001@263.net

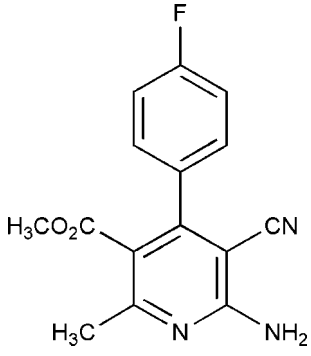
Received 24 September 2007; accepted 27 September 2007

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.006 Å; R factor = 0.065; wR factor = 0.168; data-to-parameter ratio = 12.1.

In the molecule of the title compound, $C_{15}H_{12}FN_3O_2$, the benzene and pyridine rings are oriented at a dihedral angle of 54.91 (2)°. In the crystal structure, there are intermolecular N—H···N hydrogen bonds.

Related literature

For related literature, see: Temple *et al.* (1992); Badgett & Woodward (1947); Wang *et al.* (2000); Kanbara *et al.* (1992); Tu *et al.* (2006). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{15}H_{12}FN_3O_2$
M_r = 285.27
Triclinic, $P\overline{1}$
a = 6.549 (5) Å
b = 7.658 (5) Å
c = 14.093 (10) Å
α = 81.691 (11)°
β = 86.585 (11)°
γ = 84.035 (10)°
V = 694.8 (9) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 298 (2) K
0.38 × 0.10 × 0.07 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.962, T_{max} = 0.993
3578 measured reflections
2398 independent reflections
997 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.168
S = 0.94
2398 reflections
198 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1···N1^{i}	0.90 (4)	2.17 (4)	3.063 (6)	171 (3)
N2—H2···N3^{ii}	0.86 (5)	2.26 (5)	3.099 (6)	164 (4)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1999); 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, 1999); software used to prepare material for publication: *SHELXTL*.

The authors are grateful for financial support from the National Science Foundation of China (grant No. 20672090), the Natural Science Foundation of Jiangsu Province (grant No. BK 2006033), Xuzhou Medical College (project No. 07KJ45) and Six Kinds of Professional Elite Foundation of Jiangsu Province (grant No. 06-A-039).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2330).

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  doi:10.1107/S1600536807047502

supplementary materials

Acta Cryst. (2007). E**63**, o4220 [**doi:10.1107/S1600536807047502**]

Methyl 6-amino-5-cyano-4-(4-fluorophenyl)-2-methylpyridine-3-carboxylate

Q. Wang, D. Zhou, C. Li, Q. Shao and S. Tu

Comment

Pyridine and its derivatives belong to a special class of compounds not only because of their interesting chemical and physical properties but also due to their immense utility in pharmaceutical industry (Temple *et al.*, 1992). They have been used for enrichment of cereals (Badgett & Woodward, 1947). Some polyfunctional pyridines are used as nonlinear optical (Wang *et al.*, 2000) and electrical materials (Kanbara *et al.*, 1992). We have reported the synthesis of polyfunctional pyridine derivatives (Tu *et al.*, 2006), previously, and report herein the crystal structure of the title compound, (I).

In the molecule of (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). Rings A (N1/C1—C5) and B (C7—C12) are, of course, planar and they are oriented at a dihedral angle of 54.91 (2)°.

In the crystal structure, intermolecular N—H···N hydrogen bonds (Table 1) link the molecules (Fig. 2), in which they seem to be effective in the stabilization of the structure.

Experimental

The title compound, (I), was prepared by the reaction of 4-fluorobenzaldehyde (124 mg, 1 mmol), methyl 3-aminobut-2-enoate (115 mg, 1 mmol) with malononitrile (66 mg, 1 mmol) in the solvent of ethylene glycol (1.0 ml) and acetic acid (0.5 ml) at 393 K under microwave irradiation (maximum power 200 W, initial power 100 W) for 6 min (yield; 254 mg, 89%, m.p. 552–554 K). Single crystals suitable for X-ray analysis were obtained from an ethanol solution (95%) by slow evaporation.

Refinement

H1 and H2 (for NH_2) were located in difference syntheses and refined isotropically [N—H = 0.90 (4) and 0.86 (5) Å, U_{iso}(H) = 0.038 (14) and 0.076 (19) Å^2]. The remaining H atoms were positioned geometrically, with C—H = 0.93 and 0.96 Å for aromatic and methyl H, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C), where x = 1.2 for aromatic H, and x = 1.5 for methyl H atoms.

Figures

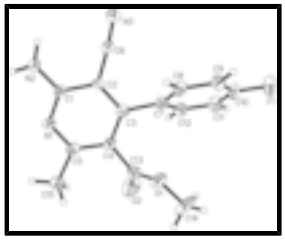

Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

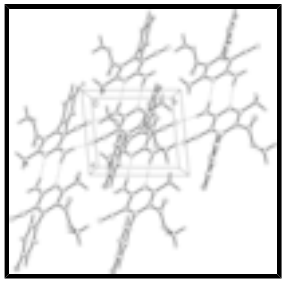

Fig. 2. A packing diagram for (I). Hydrogen bonds are shown as dashed lines.

Methyl 6-amino-5-cyano-4-(4-fluorophenyl)-2-methylpyridine-3-carboxylate

Crystal data

$C_{15}H_{12}FN_3O_2$	$Z = 2$
$M_r = 285.28$	$F_{000} = 296$
Triclinic, $P\overline{1}$	$D_x = 1.364$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 552-554 K
$a = 6.549$ (5) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 7.658$ (5) Å	Cell parameters from 542 reflections
$c = 14.093$ (10) Å	$\theta = 2.7$–26.9°
$\alpha = 81.691$ (11)°	$\mu = 0.10$ mm^{-1}
$\beta = 86.585$ (11)°	$T = 298$ (2) K
$\gamma = 84.035$ (10)°	Block, colourless
$V = 694.8$ (9) Å^3	0.38 × 0.10 × 0.07 mm

Data collection

Bruker CCD area-detector diffractometer	2398 independent reflections
Radiation source: fine-focus sealed tube	997 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.052$
$T = 298$(2) K	$\theta_{max} = 25.0^\circ$
φ and ω scans	$\theta_{min} = 1.5^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -7 \rightarrow 7$
$T_{min} = 0.962$, $T_{max} = 0.993$	$k = -9 \rightarrow 8$
3578 measured reflections	$l = -16 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.066$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.168$	$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$S = 0.94$	$(\Delta/\sigma)_{max} < 0.001$
2398 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
198 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	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 $F^2 > 2\text{sigma}(F^2)$ 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}
F1	1.1400 (5)	0.1422 (4)	0.9432 (2)	0.0852 (10)
N1	0.1942 (5)	0.5590 (4)	0.5771 (2)	0.0390 (9)
N2	0.2333 (7)	0.3171 (6)	0.4985 (3)	0.0469 (11)
N3	0.6296 (6)	0.0259 (5)	0.5904 (3)	0.0619 (13)
O1	0.6503 (6)	0.7125 (4)	0.7811 (2)	0.0593 (10)
O2	0.3267 (6)	0.7444 (5)	0.8390 (3)	0.0949 (15)
C1	0.2971 (7)	0.4024 (5)	0.5659 (3)	0.0358 (11)
C2	0.4638 (6)	0.3306 (5)	0.6242 (3)	0.0335 (11)
C3	0.5164 (6)	0.4202 (5)	0.6964 (3)	0.0367 (11)
C4	0.4060 (7)	0.5823 (5)	0.7077 (3)	0.0392 (11)
C5	0.2473 (7)	0.6473 (5)	0.6459 (3)	0.0402 (11)
C6	0.5614 (7)	0.1619 (6)	0.6082 (3)	0.0418 (12)
C7	0.6811 (7)	0.3398 (5)	0.7621 (3)	0.0368 (11)
C8	0.8750 (7)	0.2907 (5)	0.7254 (3)	0.0447 (12)
H8	0.9023	0.3030	0.6594	0.054*
C9	1.0292 (7)	0.2229 (6)	0.7878 (4)	0.0514 (13)
H9	1.1606	0.1886	0.7640	0.062*
C10	0.9864 (8)	0.2072 (6)	0.8830 (4)	0.0541 (14)
C11	0.7951 (8)	0.2497 (6)	0.9221 (3)	0.0553 (14)
H11	0.7691	0.2336	0.9882	0.066*
C12	0.6422 (7)	0.3169 (5)	0.8607 (3)	0.0486 (13)
H12	0.5107	0.3475	0.8855	0.058*
C13	0.4532 (9)	0.6880 (6)	0.7833 (4)	0.0539 (14)
C14	0.7148 (9)	0.7976 (8)	0.8582 (4)	0.100 (2)
H14A	0.8596	0.8092	0.8500	0.150*
H14B	0.6865	0.7271	0.9186	0.150*
H14C	0.6412	0.9130	0.8568	0.150*

C15	0.1249 (7)	0.8237 (6)	0.6492 (3)	0.0619 (15)
H15A	0.0245	0.8421	0.6009	0.093*
H15B	0.2153	0.9163	0.6375	0.093*
H15C	0.0567	0.8255	0.7113	0.093*
H1	0.113 (6)	0.365 (5)	0.474 (3)	0.038 (14)*
H2	0.286 (7)	0.216 (6)	0.484 (3)	0.076 (19)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.076 (2)	0.102 (2)	0.077 (2)	0.0023 (18)	−0.0401 (19)	−0.0036 (18)
N1	0.043 (2)	0.033 (2)	0.043 (2)	0.0013 (18)	−0.0063 (18)	−0.0147 (17)
N2	0.049 (3)	0.045 (3)	0.050 (3)	0.010 (2)	−0.020 (2)	−0.018 (2)
N3	0.073 (3)	0.050 (3)	0.064 (3)	0.016 (2)	−0.023 (2)	−0.021 (2)
O1	0.072 (3)	0.061 (2)	0.054 (2)	−0.0208 (19)	−0.0109 (19)	−0.0222 (17)
O2	0.080 (3)	0.132 (4)	0.085 (3)	0.011 (3)	−0.001 (2)	−0.072 (3)
C1	0.044 (3)	0.033 (3)	0.032 (3)	−0.002 (2)	0.000 (2)	−0.009 (2)
C2	0.038 (3)	0.026 (2)	0.037 (3)	−0.001 (2)	−0.003 (2)	−0.009 (2)
C3	0.043 (3)	0.037 (3)	0.030 (3)	−0.006 (2)	0.002 (2)	−0.003 (2)
C4	0.044 (3)	0.040 (3)	0.037 (3)	−0.003 (2)	−0.006 (2)	−0.013 (2)
C5	0.042 (3)	0.041 (3)	0.040 (3)	−0.004 (2)	0.003 (2)	−0.014 (2)
C6	0.045 (3)	0.042 (3)	0.041 (3)	0.001 (2)	−0.010 (2)	−0.013 (2)
C7	0.039 (3)	0.038 (3)	0.033 (3)	−0.003 (2)	−0.001 (2)	−0.007 (2)
C8	0.043 (3)	0.055 (3)	0.038 (3)	−0.008 (2)	−0.001 (3)	−0.010 (2)
C9	0.037 (3)	0.057 (3)	0.061 (4)	0.002 (3)	−0.005 (3)	−0.014 (3)
C10	0.051 (4)	0.061 (3)	0.051 (4)	−0.004 (3)	−0.024 (3)	−0.006 (3)
C11	0.069 (4)	0.061 (3)	0.035 (3)	−0.006 (3)	−0.006 (3)	−0.002 (2)
C12	0.053 (3)	0.050 (3)	0.042 (3)	0.002 (2)	−0.005 (3)	−0.009 (2)
C13	0.056 (4)	0.056 (3)	0.051 (3)	0.005 (3)	−0.011 (3)	−0.016 (3)
C14	0.130 (6)	0.112 (5)	0.082 (4)	−0.056 (4)	−0.019 (4)	−0.051 (4)
C15	0.062 (4)	0.048 (3)	0.079 (4)	0.017 (3)	−0.016 (3)	−0.032 (3)

Geometric parameters (Å, °)

F1—C10	1.362 (5)	C5—C15	1.503 (5)
N1—C1	1.339 (5)	C7—C8	1.378 (5)
N1—C5	1.341 (5)	C7—C12	1.386 (6)
N2—C1	1.336 (5)	C8—C9	1.388 (5)
N2—H1	0.90 (4)	C8—H8	0.9300
N2—H2	0.86 (5)	C9—C10	1.346 (6)
N3—C6	1.146 (5)	C9—H9	0.9300
O1—C13	1.321 (6)	C10—C11	1.365 (6)
O1—C14	1.449 (5)	C11—C12	1.372 (6)
O2—C13	1.197 (5)	C11—H11	0.9300
C1—C2	1.422 (5)	C12—H12	0.9300
C2—C3	1.385 (5)	C14—H14A	0.9600
C2—C6	1.423 (6)	C14—H14B	0.9600
C3—C4	1.395 (5)	C14—H14C	0.9600
C3—C7	1.488 (5)	C15—H15A	0.9600

C4—C5	1.400 (5)	C15—H15B	0.9600
C4—C13	1.493 (6)	C15—H15C	0.9600
C1—N1—C5	119.1 (4)	C10—C9—C8	119.2 (5)
C1—N2—H1	114 (2)	C10—C9—H9	120.4
C1—N2—H2	126 (3)	C8—C9—H9	120.4
H1—N2—H2	119 (4)	C9—C10—F1	118.5 (5)
C13—O1—C14	116.0 (4)	C9—C10—C11	123.0 (5)
N2—C1—N1	116.7 (4)	F1—C10—C11	118.5 (5)
N2—C1—C2	122.2 (4)	C10—C11—C12	117.9 (5)
N1—C1—C2	121.1 (4)	C10—C11—H11	121.1
C3—C2—C1	119.8 (4)	C12—C11—H11	121.1
C3—C2—C6	123.1 (4)	C11—C12—C7	120.9 (5)
C1—C2—C6	117.1 (4)	C11—C12—H12	119.5
C2—C3—C4	118.3 (4)	C7—C12—H12	119.5
C2—C3—C7	120.0 (4)	O2—C13—O1	124.2 (5)
C4—C3—C7	121.7 (4)	O2—C13—C4	123.8 (5)
C3—C4—C5	118.8 (4)	O1—C13—C4	112.0 (5)
C3—C4—C13	121.8 (4)	O1—C14—H14A	109.5
C5—C4—C13	119.4 (4)	O1—C14—H14B	109.5
N1—C5—C4	122.8 (4)	H14A—C14—H14B	109.5
N1—C5—C15	114.0 (4)	O1—C14—H14C	109.5
C4—C5—C15	123.1 (4)	H14A—C14—H14C	109.5
N3—C6—C2	175.0 (5)	H14B—C14—H14C	109.5
C8—C7—C12	119.4 (4)	C5—C15—H15A	109.5
C8—C7—C3	120.2 (4)	C5—C15—H15B	109.5
C12—C7—C3	120.4 (4)	H15A—C15—H15B	109.5
C7—C8—C9	119.5 (4)	C5—C15—H15C	109.5
C7—C8—H8	120.2	H15A—C15—H15C	109.5
C9—C8—H8	120.2	H15B—C15—H15C	109.5
C5—N1—C1—N2	177.7 (4)	C2—C3—C7—C8	56.5 (6)
C5—N1—C1—C2	−1.3 (6)	C4—C3—C7—C8	−126.1 (4)
N2—C1—C2—C3	−176.5 (4)	C2—C3—C7—C12	−124.9 (5)
N1—C1—C2—C3	2.5 (6)	C4—C3—C7—C12	52.5 (6)
N2—C1—C2—C6	−0.1 (6)	C12—C7—C8—C9	−1.4 (6)
N1—C1—C2—C6	178.9 (4)	C3—C7—C8—C9	177.3 (4)
C1—C2—C3—C4	−1.7 (6)	C7—C8—C9—C10	−0.3 (7)
C6—C2—C3—C4	−177.9 (4)	C8—C9—C10—F1	−179.3 (4)
C1—C2—C3—C7	175.8 (4)	C8—C9—C10—C11	2.2 (7)
C6—C2—C3—C7	−0.4 (6)	C9—C10—C11—C12	−2.2 (7)
C2—C3—C4—C5	0.0 (6)	F1—C10—C11—C12	179.3 (4)
C7—C3—C4—C5	−177.4 (4)	C10—C11—C12—C7	0.4 (7)
C2—C3—C4—C13	−179.7 (4)	C8—C7—C12—C11	1.4 (7)
C7—C3—C4—C13	2.8 (7)	C3—C7—C12—C11	−177.3 (4)
C1—N1—C5—C4	−0.5 (6)	C14—O1—C13—O2	6.5 (7)
C1—N1—C5—C15	178.2 (4)	C14—O1—C13—C4	−173.8 (4)
C3—C4—C5—N1	1.1 (6)	C3—C4—C13—O2	−128.8 (5)
C13—C4—C5—N1	−179.1 (4)	C5—C4—C13—O2	51.4 (7)
C3—C4—C5—C15	−177.4 (4)	C3—C4—C13—O1	51.5 (6)

C13—C4—C5—C15	2.4 (7)	C5—C4—C13—O1	−128.3 (4)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1···N1^{i}	0.90 (4)	2.17 (4)	3.063 (6)	171 (3)
N2—H2···N3^{ii}	0.86 (5)	2.26 (5)	3.099 (6)	164 (4)

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

Fig. 1

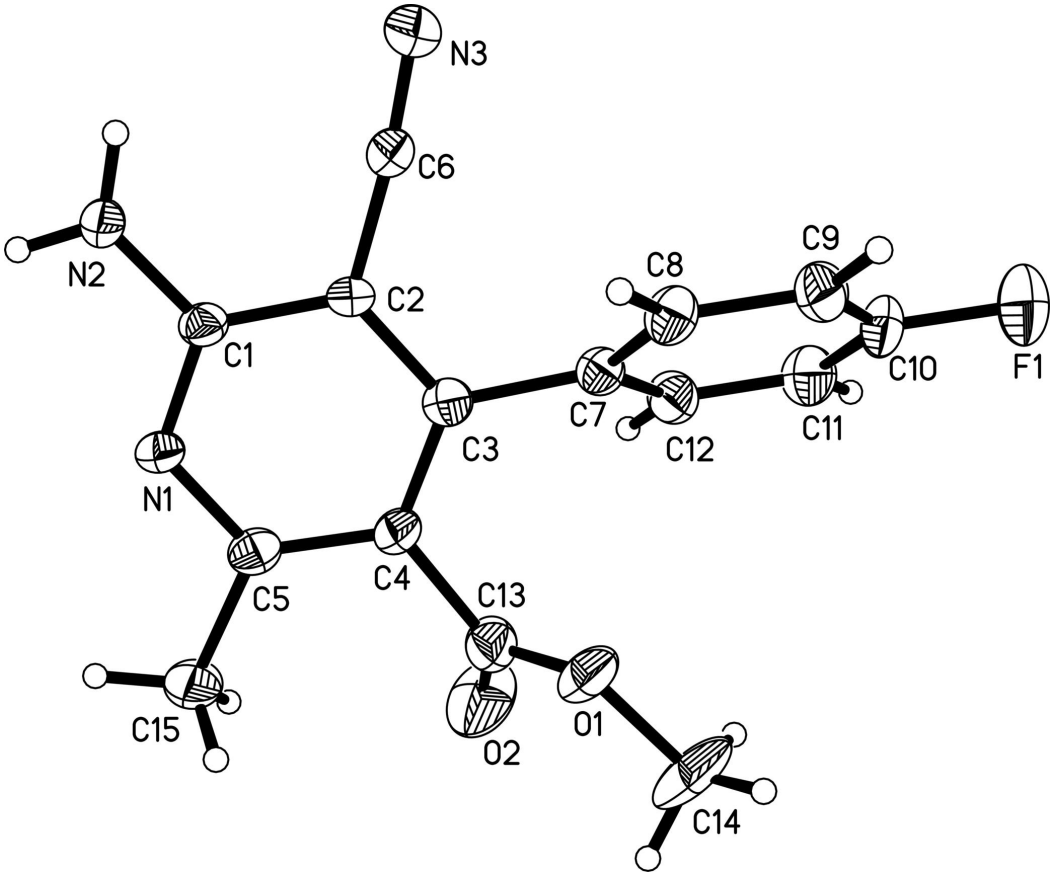

Fig. 2