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Ethyl 4-amino-5-cyano-2-methyl-6-(2-nitrophenoxy)nicotinate

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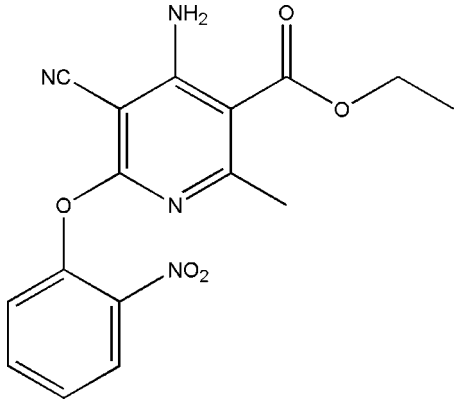
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.003 Å; R factor = 0.049; wR factor = 0.167; data-to-parameter ratio = 13.4.

In the title compound, $C_{16}H_{14}N_4O_5$, the benzene ring of the nicotinate residue is inclined at an angle of 64.06 (10)° to the benzene ring of the nitrophenoxy group. The molecules are linked by two intermolecular C—H···O and N—H···N hydrogen bonds into a complex three-dimensional framework structure. C—H···π interactions also contribute to the stability of the crystal packing.

Related literature

For the biological importance of nicotine derivatives, see Yildiz (2004). For reference structural data, see Allen *et al.* (1987).



Experimental

Crystal data

$C_{16}H_{14}N_4O_5$
M_r = 342.31
Triclinic, $P\overline{1}$
a = 7.9831 (6) Å
b = 8.8661 (7) Å
c = 12.2797 (10) Å
α = 69.012 (1)°
β = 86.342 (1)°
γ = 88.835 (1)°
V = 809.83 (11) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 294 (2) K
0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: none
8410 measured reflections
3145 independent reflections
2146 reflections with $I > 2\sigma(I)$
R_{int} = 0.023

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.167
S = 1.07
3145 reflections
235 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

*Cg*1 is the centroid of the N1/C4/C3/C2/C1/C5 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7B···O4^{i}	0.97	2.52	3.229 (3)	130
N2—H2A···N3^{ii}	0.86 (2)	2.23 (2)	3.040 (3)	157.5 (19)
N2—H2B···O1	0.92 (2)	1.84 (2)	2.593 (2)	137.1 (18)
C7—H7B···Cg1^{i}	0.97	2.92	3.716 (3)	140

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2001).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2374).

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supplementary materials

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Ethyl 4-amino-5-cyano-2-methyl-6-(2-nitrophenoxy)nicotinate

Q.-Y. Ren, H.-W. He, Y.-Y. Yao and Y.-C. Gu

Comment

Pyridine derivatives are important compounds because of their presence in numerous natural products. For example, nicotine is found in a wide variety of plants, which play important roles in metabolism and possess a wide spectrum of biological activity (Yildiz, 2004). We report here the molecular structure of the nicotinate derivative (I) (Fig. 1). In the title compound, all bond lengths and angles are within normal ranges (Allen *et al.*, 1987) and the molecules are linked by two intermolecular C—H···O and N—H···N hydrogen bonds into a complex three-dimensional framework structure (Fig. 2). Weak C—H···π interactions (Table 1, *Cg* is a centroid of the N1/C4/C3/C2/C1/C5 ring) also contribute to the crystal packing stability.

Experimental

A mixture of 4-amino-5-cyano-6-methanesulfonyl-2-methyl-nicotinic acid ethyl ester (1.4 g, 5 mmol) and catalytic solid K_2CO_3 (0.012 g, 0.1 mmol) were added to a solution of 2-nitro-phenol (0.7 g, 5 mmol) in anhydrous ethanol (20 ml), stirred for 2 h at 341 K and filtered. The filtrate was condensed and the residue recrystallized from dichloromethane/ petroleum ether to give pure 4-amino-5-cyano-2-methyl-6-(2-nitro-phenoxy)-nicotinic acid ethyl ester (yield 86%). Crystals of (I) suitable for X-ray structure analysis were grown from ethanol.

Refinement

Amine H atoms were refined with fixed isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(N)$. All other H atoms were placed in calculated positions, with C—H distances in the range 0.93–0.97 Å and refined using a riding-model approximation, with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$.

Figures

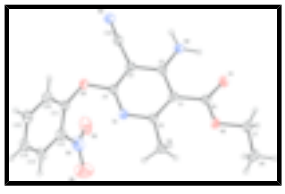

Fig. 1. The structure of (I). showing 50% probability displacement ellipsoids and the atom-numbering scheme.

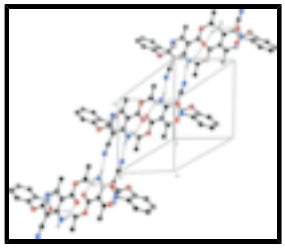

Fig. 2. Part of the crystal packing of (I) showing the formation of dimers linked by hydrogen-bonds (dashed lines).

Ethyl 4-amino-5-cyano-2-methyl-6-(2-nitrophenoxy)nicotinate

Crystal data

$C_{16}H_{14}N_4O_5$	$Z = 2$
$M_r = 342.31$	$F_{000} = 356$
Triclinic, $P\overline{1}$	$D_x = 1.404$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.9831$ (6) Å	Cell parameters from 2185 reflections
$b = 8.8661$ (7) Å	$\theta = 2.5$–24.8º
$c = 12.2797$ (10) Å	$\mu = 0.11$ mm^{-1}
$\alpha = 69.012$ (1)º	$T = 294$ (2) K
$\beta = 86.342$ (1)º	Block, yellow
$\gamma = 88.835$ (1)º	0.30 × 0.20 × 0.20 mm
$V = 809.83$ (11) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2146 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.023$
Monochromator: graphite	$\theta_{max} = 26.0$º
$T = 294$(2) K	$\theta_{min} = 1.8$º
φ and ω scans	$h = -9\rightarrow9$
Absorption correction: none	$k = -9\rightarrow10$
8410 measured reflections	$l = -15\rightarrow15$
3145 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.167$	$w = 1/[\sigma^2(F_o^2) + (0.0992P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
3145 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
235 parameters	$\Delta\rho_{min} = -0.20$ 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}
C1	0.2580 (2)	0.4848 (2)	0.52656 (15)	0.0386 (4)
C2	0.3286 (2)	0.6325 (2)	0.52562 (14)	0.0370 (4)
C3	0.3988 (2)	0.6298 (2)	0.62939 (15)	0.0395 (4)
C4	0.3964 (2)	0.4853 (2)	0.72421 (15)	0.0410 (5)
C5	0.2584 (2)	0.3490 (2)	0.63016 (15)	0.0406 (5)
C6	0.1914 (2)	0.4850 (2)	0.41669 (15)	0.0410 (5)
C7	0.0793 (3)	0.3396 (3)	0.31026 (17)	0.0582 (6)
H7A	0.1691	0.3657	0.2494	0.070*
H7B	−0.0098	0.4180	0.2844	0.070*
C8	0.0149 (3)	0.1740 (3)	0.3342 (2)	0.0666 (7)
H8A	0.1043	0.0976	0.3587	0.100*
H8B	−0.0281	0.1683	0.2645	0.100*
H8C	−0.0733	0.1492	0.3949	0.100*
C9	0.1826 (3)	0.1880 (2)	0.64853 (17)	0.0545 (6)
H9A	0.2494	0.1351	0.6051	0.082*
H9B	0.0707	0.2029	0.6221	0.082*
H9C	0.1790	0.1227	0.7301	0.082*
C10	0.4724 (2)	0.7727 (2)	0.63351 (15)	0.0444 (5)
C11	0.4771 (3)	0.3499 (2)	0.91776 (16)	0.0470 (5)
C12	0.3363 (3)	0.2736 (3)	0.98573 (16)	0.0536 (6)
C13	0.3529 (3)	0.1356 (3)	1.08299 (17)	0.0643 (6)
H13	0.2578	0.0829	1.1267	0.077*
C14	0.5091 (3)	0.0763 (3)	1.11508 (18)	0.0649 (7)
H14	0.5206	−0.0165	1.1806	0.078*
C15	0.6482 (3)	0.1545 (3)	1.05021 (19)	0.0659 (7)
H15	0.7544	0.1158	1.0729	0.079*
C16	0.6325 (3)	0.2898 (3)	0.95177 (17)	0.0569 (6)
H16	0.7281	0.3409	0.9079	0.068*
N1	0.3292 (2)	0.35024 (18)	0.72735 (13)	0.0438 (4)
N2	0.3315 (2)	0.7694 (2)	0.43277 (15)	0.0493 (5)
H2A	0.376 (3)	0.855 (3)	0.4358 (18)	0.059*
H2B	0.280 (3)	0.763 (2)	0.3694 (18)	0.059*
N3	0.5293 (3)	0.8913 (2)	0.63011 (14)	0.0612 (5)

O1	0.1840 (2)	0.60489 (18)	0.32916 (12)	0.0663 (5)
O2	0.14144 (18)	0.34349 (16)	0.41824 (11)	0.0534 (4)
O3	0.47215 (18)	0.49029 (15)	0.81893 (11)	0.0531 (4)
N4	0.1667 (3)	0.3358 (4)	0.95640 (18)	0.0800 (7)
O4	0.1477 (2)	0.4784 (3)	0.90715 (17)	0.0958 (7)
O5	0.0543 (3)	0.2366 (4)	0.9836 (3)	0.1476 (12)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0385 (10)	0.0368 (10)	0.0419 (10)	0.0019 (8)	−0.0053 (8)	−0.0154 (8)
C2	0.0370 (10)	0.0324 (10)	0.0394 (9)	−0.0006 (8)	−0.0006 (7)	−0.0105 (8)
C3	0.0416 (11)	0.0341 (10)	0.0432 (10)	−0.0005 (8)	−0.0042 (8)	−0.0140 (8)
C4	0.0424 (11)	0.0408 (11)	0.0404 (10)	0.0002 (8)	−0.0074 (8)	−0.0146 (9)
C5	0.0417 (11)	0.0354 (11)	0.0441 (10)	0.0013 (8)	−0.0072 (8)	−0.0130 (8)
C6	0.0423 (11)	0.0376 (11)	0.0425 (10)	−0.0002 (8)	−0.0053 (8)	−0.0131 (9)
C7	0.0720 (15)	0.0594 (14)	0.0481 (11)	−0.0071 (11)	−0.0169 (10)	−0.0227 (10)
C8	0.0756 (16)	0.0589 (15)	0.0743 (15)	−0.0113 (12)	−0.0163 (12)	−0.0322 (12)
C9	0.0711 (14)	0.0367 (11)	0.0512 (11)	−0.0104 (10)	−0.0162 (10)	−0.0074 (9)
C10	0.0547 (12)	0.0395 (12)	0.0390 (10)	−0.0004 (9)	−0.0093 (9)	−0.0130 (9)
C11	0.0591 (13)	0.0450 (12)	0.0383 (10)	−0.0033 (10)	−0.0112 (9)	−0.0149 (9)
C12	0.0527 (13)	0.0674 (14)	0.0428 (10)	0.0028 (11)	−0.0069 (9)	−0.0217 (10)
C13	0.0697 (16)	0.0748 (16)	0.0397 (11)	−0.0108 (13)	0.0027 (10)	−0.0105 (11)
C14	0.0813 (17)	0.0661 (15)	0.0391 (11)	0.0015 (13)	−0.0136 (11)	−0.0074 (10)
C15	0.0618 (15)	0.0741 (16)	0.0554 (13)	0.0050 (12)	−0.0206 (11)	−0.0128 (12)
C16	0.0514 (12)	0.0630 (14)	0.0502 (11)	−0.0086 (11)	−0.0118 (9)	−0.0109 (10)
N1	0.0500 (10)	0.0372 (9)	0.0434 (8)	−0.0004 (7)	−0.0106 (7)	−0.0122 (7)
N2	0.0650 (12)	0.0354 (10)	0.0452 (9)	−0.0090 (8)	−0.0114 (8)	−0.0098 (8)
N3	0.0888 (14)	0.0410 (11)	0.0522 (10)	−0.0149 (10)	−0.0131 (9)	−0.0123 (8)
O1	0.1016 (12)	0.0464 (9)	0.0463 (8)	−0.0109 (8)	−0.0231 (8)	−0.0073 (7)
O2	0.0730 (10)	0.0426 (8)	0.0482 (8)	−0.0033 (7)	−0.0205 (7)	−0.0175 (6)
O3	0.0704 (10)	0.0435 (8)	0.0447 (7)	−0.0063 (7)	−0.0205 (7)	−0.0119 (6)
N4	0.0603 (14)	0.109 (2)	0.0623 (13)	0.0128 (14)	−0.0020 (10)	−0.0218 (13)
O4	0.0948 (15)	0.1149 (17)	0.0783 (12)	0.0484 (13)	−0.0232 (10)	−0.0348 (12)
O5	0.0550 (14)	0.171 (3)	0.174 (3)	−0.0182 (16)	−0.0053 (14)	−0.010 (2)

Geometric parameters (Å, °)

C1—C5	1.404 (2)	C9—H9A	0.9600
C1—C2	1.431 (2)	C9—H9B	0.9600
C1—C6	1.481 (2)	C9—H9C	0.9600
C2—N2	1.335 (2)	C10—N3	1.140 (2)
C2—C3	1.417 (2)	C11—C16	1.371 (3)
C3—C4	1.388 (2)	C11—C12	1.387 (3)
C3—C10	1.425 (3)	C11—O3	1.395 (2)
C4—N1	1.309 (2)	C12—C13	1.381 (3)
C4—O3	1.359 (2)	C12—N4	1.469 (3)
C5—N1	1.356 (2)	C13—C14	1.369 (3)
C5—C9	1.497 (3)	C13—H13	0.9300

C6—O1	1.215 (2)	C14—C15	1.368 (3)
C6—O2	1.318 (2)	C14—H14	0.9300
C7—O2	1.457 (2)	C15—C16	1.375 (3)
C7—C8	1.486 (3)	C15—H15	0.9300
C7—H7A	0.9700	C16—H16	0.9300
C7—H7B	0.9700	N2—H2A	0.86 (2)
C8—H8A	0.9600	N2—H2B	0.92 (2)
C8—H8B	0.9600	N4—O4	1.201 (3)
C8—H8C	0.9600	N4—O5	1.214 (3)
C5—C1—C2	118.42 (15)	H9A—C9—H9B	109.5
C5—C1—C6	124.14 (17)	C5—C9—H9C	109.5
C2—C1—C6	117.43 (15)	H9A—C9—H9C	109.5
N2—C2—C3	119.45 (16)	H9B—C9—H9C	109.5
N2—C2—C1	123.34 (16)	N3—C10—C3	176.00 (18)
C3—C2—C1	117.21 (15)	C16—C11—C12	118.77 (18)
C4—C3—C2	118.35 (16)	C16—C11—O3	116.93 (18)
C4—C3—C10	121.79 (16)	C12—C11—O3	124.21 (18)
C2—C3—C10	119.85 (16)	C13—C12—C11	120.4 (2)
N1—C4—O3	119.80 (16)	C13—C12—N4	118.3 (2)
N1—C4—C3	125.17 (16)	C11—C12—N4	121.4 (2)
O3—C4—C3	115.03 (16)	C14—C13—C12	120.0 (2)
N1—C5—C1	122.69 (17)	C14—C13—H13	120.0
N1—C5—C9	111.75 (15)	C12—C13—H13	120.0
C1—C5—C9	125.56 (16)	C15—C14—C13	119.6 (2)
O1—C6—O2	120.82 (16)	C15—C14—H14	120.2
O1—C6—C1	123.74 (17)	C13—C14—H14	120.2
O2—C6—C1	115.44 (15)	C14—C15—C16	120.7 (2)
O2—C7—C8	107.72 (16)	C14—C15—H15	119.7
O2—C7—H7A	110.2	C16—C15—H15	119.7
C8—C7—H7A	110.2	C11—C16—C15	120.5 (2)
O2—C7—H7B	110.2	C11—C16—H16	119.8
C8—C7—H7B	110.2	C15—C16—H16	119.8
H7A—C7—H7B	108.5	C4—N1—C5	118.08 (15)
C7—C8—H8A	109.5	C2—N2—H2A	120.3 (14)
C7—C8—H8B	109.5	C2—N2—H2B	114.6 (13)
H8A—C8—H8B	109.5	H2A—N2—H2B	125 (2)
C7—C8—H8C	109.5	C6—O2—C7	116.55 (14)
H8A—C8—H8C	109.5	C4—O3—C11	118.84 (15)
H8B—C8—H8C	109.5	O4—N4—O5	124.5 (3)
C5—C9—H9A	109.5	O4—N4—C12	119.0 (2)
C5—C9—H9B	109.5	O5—N4—C12	116.5 (2)
C5—C1—C2—N2	−178.52 (17)	O3—C11—C12—N4	1.1 (3)
C6—C1—C2—N2	2.4 (3)	C11—C12—C13—C14	2.2 (3)
C5—C1—C2—C3	1.8 (3)	N4—C12—C13—C14	−178.2 (2)
C6—C1—C2—C3	−177.30 (15)	C12—C13—C14—C15	−0.1 (3)
N2—C2—C3—C4	−179.08 (17)	C13—C14—C15—C16	−1.5 (4)
C1—C2—C3—C4	0.6 (3)	C12—C11—C16—C15	1.3 (3)
N2—C2—C3—C10	−0.3 (3)	O3—C11—C16—C15	178.09 (19)

C1—C2—C3—C10	179.41 (16)	C14—C15—C16—C11	0.8 (4)
C2—C3—C4—N1	−2.3 (3)	O3—C4—N1—C5	−178.43 (16)
C10—C3—C4—N1	178.96 (18)	C3—C4—N1—C5	1.2 (3)
C2—C3—C4—O3	177.40 (16)	C1—C5—N1—C4	1.5 (3)
C10—C3—C4—O3	−1.4 (3)	C9—C5—N1—C4	−178.27 (16)
C2—C1—C5—N1	−2.9 (3)	O1—C6—O2—C7	0.5 (3)
C6—C1—C5—N1	176.06 (16)	C1—C6—O2—C7	−178.49 (16)
C2—C1—C5—C9	176.76 (18)	C8—C7—O2—C6	−174.60 (17)
C6—C1—C5—C9	−4.2 (3)	N1—C4—O3—C11	0.3 (3)
C5—C1—C6—O1	176.23 (18)	C3—C4—O3—C11	−179.36 (16)
C2—C1—C6—O1	−4.8 (3)	C16—C11—O3—C4	118.4 (2)
C5—C1—C6—O2	−4.8 (3)	C12—C11—O3—C4	−64.9 (3)
C2—C1—C6—O2	174.18 (15)	C13—C12—N4—O4	150.4 (2)
C16—C11—C12—C13	−2.8 (3)	C11—C12—N4—O4	−30.0 (3)
O3—C11—C12—C13	−179.35 (17)	C13—C12—N4—O5	−30.2 (3)
C16—C11—C12—N4	177.6 (2)	C11—C12—N4—O5	149.4 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7B···O4^{i}	0.97	2.52	3.229 (3)	130
N2—H2A···N3^{ii}	0.86 (2)	2.23 (2)	3.040 (3)	157.5 (19)
N2—H2B···O1	0.92 (2)	1.84 (2)	2.593 (2)	137.1 (18)
C7—H7B···Cg1^{i}	0.97	2.92	3.716 (3)	140

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

Fig. 1

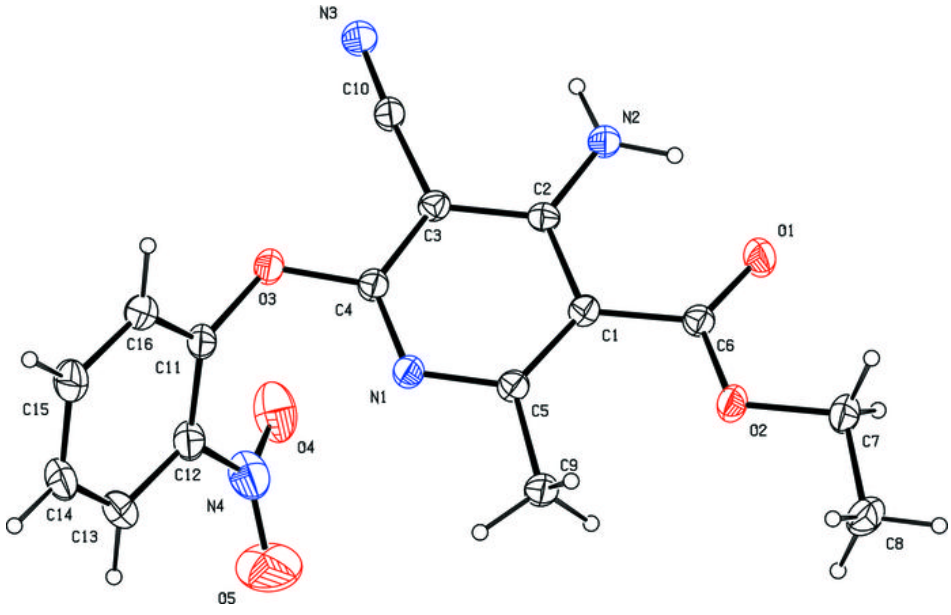
N3
C10
N2
C2
C3
O1
O3
C4
C1
C6
C16
C11
N1
C5
O2
C7
C15
O4
C12
C9
C14
N4
C13
C8
O5

Fig. 2