



Ethyl 2-amino-1-(4-fluorophenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate: crystal structure and Hirshfeld surface analysis

U. H. Patel,^a Chintan Jotaniya,^{b*} D. A. Shah^c and Bhavesh Socha^b

^aDepartment of Physics, V.V. Nagar, Anand, Gujarat, India, ^b103, X-Ray Lab, Department of Physics, V.V. Nagar, Anand, Gujarat, India, and ^cOrganic Synthesis Laboratory, M. G. Science Institute, Ahmedabad, Gujarat, India. *Correspondence e-mail: chintan.jotaniya@gmail.com

Received 23 June 2017
Accepted 8 August 2017

Edited by P. Dastidar, Indian Association for the Cultivation of Science, India

Keywords: crystal structure; halogen-substituted pyrrole derivative; X-ray crystallography; Hirshfeld surface analysis; hydrogen bonding.

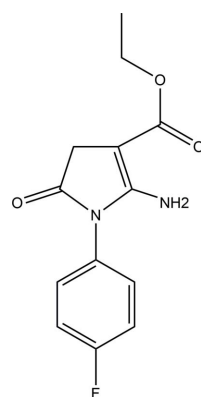
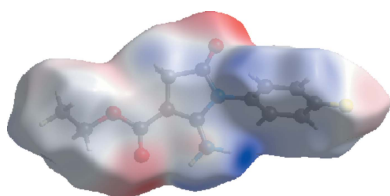
CCDC reference: 1555656

Supporting information: this article has supporting information at journals.iucr.org/e

In the title molecule, C₁₂H₁₃FN₂O₃, the central pyrrole ring makes a dihedral angle of 9.2 (3)° with the ethoxy carbonyl moiety whereas the fluorophenyl ring is rotated by 67.6 (2)° from the pyrrole ring. Supramolecular aggregation is due to off-centric π–π stacking interactions involving screw-related pairs of molecules, which are further connected by N–H···O and C–H···O interactions, forming a sinusoidal pattern along the [001] direction on the *bc* plane. Three-dimensional Hirshfeld surface analysis and two-dimensional fingerprint plots confirm the contributions of these interactions.

1. Chemical context

Pyrrole, an electron-rich five-membered unsaturated ring, and its derivatives are widely used as intermediates in the synthesis of organic compounds, medicines, pharmaceuticals, agrochemicals, perfumes *etc.* Its derivatives possess a broad spectrum of biological activities. Substitution by a halogen (Cl, Br, F, I) is known to increase the activities of drug molecules and this group of molecules interact with receptors *via* halogen bonding. Organofluorine compounds display a variety of pharmacological and agro-chemical properties. Specific halogen-bonding interactions are responsible for the supramolecular architecture in halogen-substituted heterocycles. Bearing in mind the importance of pyrrole and the role of halogens, we have synthesized a series of halogen-substituted pyrrole derivatives. Bromo and methoxy derivatives of the title molecule have been reported earlier (Patel *et al.*, 2012, 2013). As a continuation of these studies, the title molecule, with fluorine as one of the substituents, was synthesized and characterized crystallographically and by Hirshfeld surface analysis.



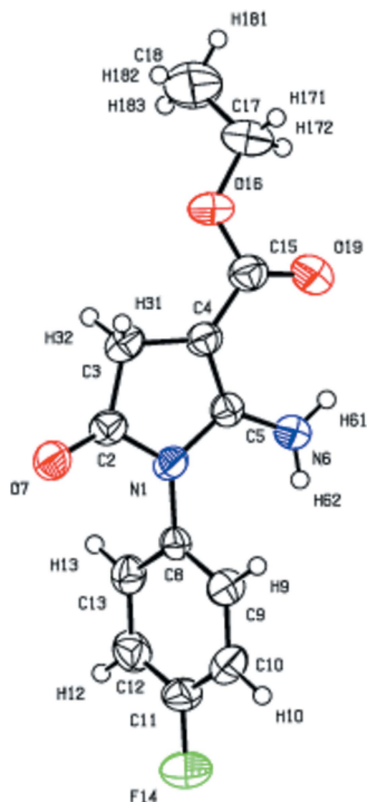


Figure 1
ORTEP view of the title molecule with the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level.

2. Structural commentary

In the title compound, Fig. 1, the F atom is displaced by 0.014 (3) Å from the phenyl ring, facilitating it in to take part in a number of intermolecular interactions. The heterocyclic five-membered pyrrole ring is essentially planar with a maximum displacement of 0.022 (4) Å for atom C3 from its mean plane. The fluorophenyl ring forms a dihedral angle of 67.6 (2)° whereas the mean plane of ethoxy carbonyl tail is

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

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N6—H61···O19	0.86	2.2400	2.806 (4)	123
N6—H62···O7 ⁱ	0.86	2.2100	2.970 (4)	147
C13—H13···O7 ⁱⁱ	0.93	2.6000	3.320 (5)	135

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

inclined at 9.2 (3)° to the central pyrrole ring. The terminal ethoxy carbonyl chain adopts a zigzag extended conformation, as is usually observed in analogous derivatives, with the carbonyl oxygen atom O19 on the same side as the methyl carbon atom C17 [C17—O16—C15—O19 = 5.0 (7)°] and the ethoxy carbon atom C18 in a *trans* [C15—O16—C17—C18 = 144.6 (5)°] conformation with respect to the pyrrole ring. Bond lengths in the phenyl ring vary from 1.365 (6) to 1.385 (6) Å and the endocyclic angle varies from 118.0 (4) to 122.9 (4)° with an average value of 120.4 (4)°, which coincides exactly with the theoretical value 120° for sp^2 hybridization.

The intramolecular N6—H61···O19 hydrogen bond involving the carbonyl oxygen atom O19 leads to the formation of a pseudo-six-membered ring with an *S*(6) graph-set motif.

3. Supramolecular features

In the crystal, two pairs of screw-related molecules are held together by off-centric π – π stacking interactions involving the pyrrole ring and the phenyl ring of a screw-related molecule ($-x, \frac{1}{2} + y, \frac{1}{2} - z$) [centroid–centroid distance = 4.179 (2) Å, slippage = 2.036 Å, dihedral angle between planes = 5.9 (2)°], forming chains along [010]. The structure contains infinite zigzag chains of screw-related molecules, forming a sinusoidal patterns along [001] on the *bc* plane as shown in Fig. 2.

The molecular packing features N—H···O interactions, which lead to the formation of chains along [001], and π – π stacking interactions, which link the molecules along [010]. In

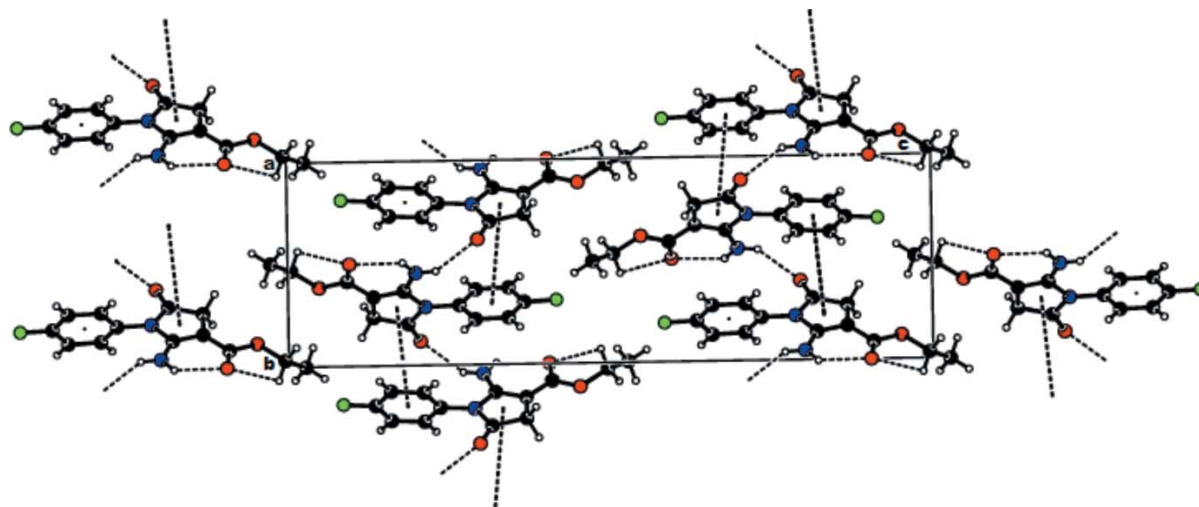


Figure 2
View of the packing showing π – π stacking interactions and N—H···O and C—H···O hydrogen bonds (dashed lines) in the *bc* plane.

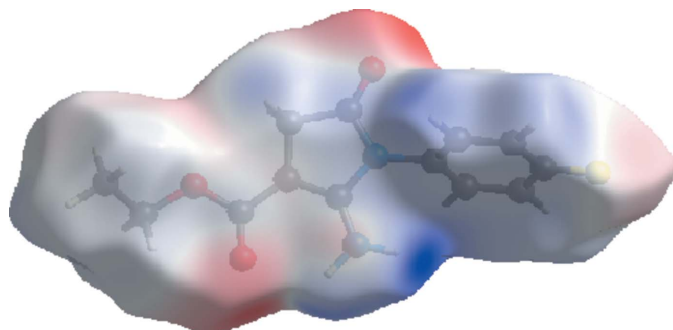


Figure 3
View of the Hirshfeld surface mapped over the calculated electrostatic potential for the title compound. The red and blue regions represent negative and positive electrostatic potentials, respectively.

addition, C—H1···O interactions stack the molecules along [100] (Fig. 2, Table 1).

4. Analysis of the Hirshfeld Surfaces

Crystal Explorer 3.1 (Wolff *et al.*, 2012) was used to generate Hirshfeld surfaces mapped over d_{norm} , d_{e} and electrostatic potential for the title compound. The electrostatic potentials were calculated using *TONTO* (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005) as integrated in *Crystal Explorer* and are mapped on Hirshfeld surfaces using the STO-3G basis set at the Hartree–Fock level of theory over a range ± 0.10 au as shown in Fig. 3. The positive electrostatic potential (blue region) over the surface indicates a hydrogen-bond donor, whereas the hydrogen-bond acceptors are represented by negative electrostatic potential (red region). The contact distances d_{i} and d_{e} from the Hirshfeld surface to the nearest atom inside and outside, respectively, enables the analysis of the intermolecular interactions through the mapping of d_{norm} .

A view of the Hirshfeld surface mapped over d_{norm} , shape-index and curvedness for the title compound are shown in Fig. 4. Hirshfeld surfaces marked with red regions in d_{norm} near atoms O7, O19, N6, H62 and H10 reveal the active participation of the respective atoms in intermolecular interactions. The occurrence of N—H···O and C—H···O interactions is confirmed by analysis of the Hirshfeld surface. N6—H62···O19 interactions are shown on the Hirshfeld surface marked with bright-red dotted lines in Fig. 5. Yellow dotted lines mapped on the d_{norm} Hirshfeld surface in Fig. 6 reveal the

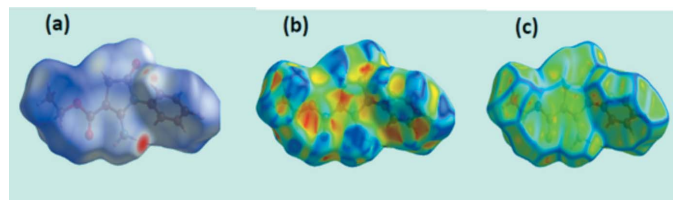


Figure 4
View of the Hirshfeld surface mapped over (a) d_{norm} , (b) shape-index and (c) curvedness.

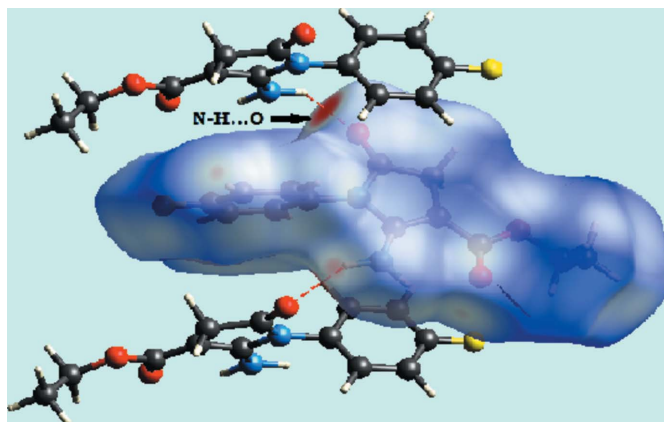


Figure 5
 d_{norm} mapped on the Hirshfeld surface for visualizing the N—H···O intermolecular interactions of the title compound. Red dotted lines represent hydrogen bonds.

presence of C13—H13···O7 and C17—H172···O19 interactions.

The two-dimensional fingerprint plots (Rohl *et al.*, 2008) for the title molecule are shown in Fig. 7. The inter atomic H···H contacts appear as scattered points over the larger part of the plot along with one distinct spike with the highest contribution within the Hirshfeld surface of 44.9% (Fig. 7*b*), followed by 20.8% for O···H/H···O contacts, which appear as pairs of adjacent spikes having almost same length. The contributions of H···F/F···H and C···H/H···C contacts are 12.8 and 10.4%, respectively. The contribution of C···C contacts, *i.e.* 3.0%, shows the π – π stacking interactions in the compound have a relatively smaller contribution. Apart from these, C···O/O···C, C···N/N···C, O···F/F···O, O···N/N···O and C···F/F···C contacts are found, as summarized in Table 2.

5. Database survey

Two analogous structures, 2-amino-1(4-bromophenyl)-5-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylic acid ethyl ester (Patel *et*

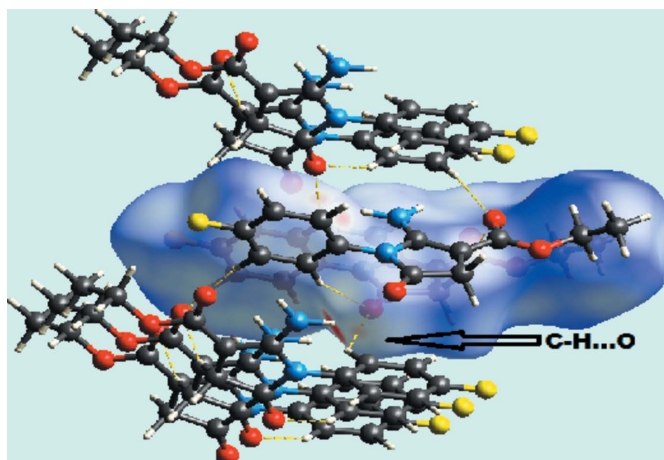


Figure 6
 d_{norm} mapped on the Hirshfeld surface for visualizing the C—H···O intermolecular interactions (yellow dotted lines) of the title compound.

Table 2

Summary of various contacts and their percentage contributions to the Hirshfeld surface.

Type of contact	Contribution
H...H	44.9
O...H/H...O	20.8
H...F/F...H	12.8
C...H/H...C	10.4
C...C	3.4
C...O/O...C	3.0
C...N/N...C	1.8
O...F/F...O	1.0
O...N/N...O	0.6
C...F/F...C	0.5

al., 2012) and 2-amino-1-(4-methoxyphenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylic acid ethyl ester (Patel *et al.*, 2013), in which the fluorophenyl ring of the title compound is replaced by a bromo or methoxyphenyl ring, are reported in the Cambridge Structural Database (Groom *et al.*, 2016).

6. Synthesis and crystallization

In a 50 ml flat-bottom flask, a mixture of dry toluene (15 ml), potassium hydroxide (0.012 mol, 0.672 g) and 18-crown-6 (0.0005 mol, 0.132 g) were prepared. Ethyl cyanoacetate (0.006 mol, 0.6787 g) was then added to this stirred mixture, followed by the portionwise addition of *N*-(4-fluorophenyl)-2-chloroacetamide (0.005 mol, 1.2425 g) after 5 min. The stirring was continued until the chloroacetamide derivative had been consumed (20 min), monitored TLC (hexane:ethyl acetate 7:3). On completion of the reaction, water (25 ml) was added to the reaction mixture and stirring continued for a further

Table 3

Experimental details.

Crystal data	
Chemical formula	C ₁₃ H ₁₃ FN ₂ O ₃
<i>M_r</i>	264.25
Crystal system, space group	Orthorhombic, <i>P</i> ₂ ₁ 2 ₁
Temperature (K)	273
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.5357 (16), 8.548 (2), 27.026 (7)
<i>V</i> (Å ³)	1278.9 (6)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.7 × 0.3 × 0.2
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2007)
<i>T_{min}</i> , <i>T_{max}</i>	0.962, 0.979
No. of measured, independent and observed [<i>I</i> > 2Σ(<i>I</i>)] reflections	7696, 2975, 2322
<i>R_{int}</i>	0.032
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.075, 0.148, 1.18
No. of reflections	2975
No. of parameters	173
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.23, -0.24

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

5 min. This was then taken into a separating funnel and the aqueous phase was neutralized with glacial acetic acid (pH = 7). The phases were separated and the aqueous phase extracted with toluene (10 ml). The combined organic layers were dried over magnesium sulfate and the toluene removed

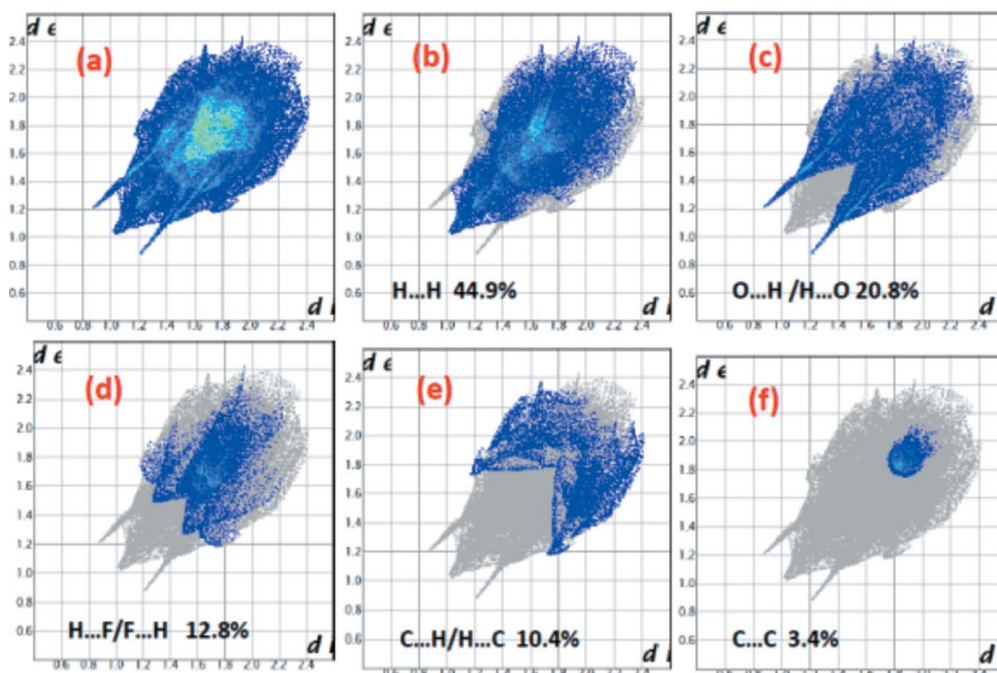


Figure 7

The two-dimensional fingerprint plots for the title compound, showing contributions from different contacts, (a) all, (b) H...H, (c) O...H/H...O, (d) H...F/F...H, (e) C...H/H...C and (f) C...C, respectively.

in vacuo to obtain a solid product. The crude product was crystallized from ethanol to obtain 1.42 g (87% yield) of 2-amino-1-(4-fluorophenyl)-oxo-4,5-dihydro-1*H*-pyrrole-3-carboxylic acid ethyl ester, m.p. 783.24 K. It is more or less soluble in different solvents such as benzene, ethanol, DMF, DMSO, CH₂Cl₂, CHCl₃, ethyl acetate but diffraction quality crystal could be grown by the slow evaporation method at room temperature from ethyl acetate only after repeated trials.

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. Carbon-bound H atoms were placed in their calculated positions (C–H = 0.93–0.97 Å) and are included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

Acknowledgements

The authors are thankful to the Department of Physics, SPU, for providing the financial support to carry out the work and also to CSMCRI, Bhavnagar, for the data collection.

References

- Bruker (2007). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Jayatilaka, D., Grimwood, D. J., Lee, A., Lemay, A., Russel, A. J., Taylor, C., Wolff, S. K., Cassam-Chenai, P. & Whitton, A. (2005). *TONTO – A System for Computational Chemistry*. Available at: <http://hirshfeldsurface.net/>
- Patel, B. D., Patel, U. H. & Shah, D. A. (2012). *Int. J. Appl. Sci. Eng. Res.* **1**, 6, 755–762.
- Patel, U. H., Patel, B. D. & Shah, D. A. (2013). *Int. J. Appl. Sci. Eng. Res.* **2**, 170–180.
- Rohl, A. L., Moret, M., Kaminsky, W., Claborn, K., McKinnon, J. J. & Kahr, B. (2008). *Cryst. Growth Des.* **8**, 4517–4525.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A., McKinnon, J. J. & Jayatilaka, D. (2008). *CrystEngComm*, **10**, 377–388.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Turner, M. J., Jayatilaka, D. & Spackman, M. A. (2012). *Crystal Explorer*. The University of Western Australia.

supporting information

Acta Cryst. (2017). E73, 1336-1340 [https://doi.org/10.1107/S2056989017011628]

Ethyl 2-amino-1-(4-fluorophenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate: crystal structure and Hirshfeld surface analysis

U. H. Patel, Chintan Jotaniya, D. A. Shah and Bhavesh Socha

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Ethyl 2-amino-1-(4-fluorophenyl)-5-oxo-4,5-dihydro-1H-pyrrole-3-carboxylate:

Crystal data

$C_{13}H_{13}FN_2O_3$

$M_r = 264.25$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 5.5357$ (16) Å

$b = 8.548$ (2) Å

$c = 27.026$ (7) Å

$V = 1278.9$ (6) Å³

$Z = 4$

$F(000) = 552$

$D_x = 1.372$ Mg m⁻³

Melting point: 783.39 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7696 reflections

$\theta = 1.5$ – 28.2°

$\mu = 0.11$ mm⁻¹

$T = 273$ K

Transparent, colourless

$0.7 \times 0.3 \times 0.2$ mm

Data collection

Bruker SMART APEX CCD
diffractometer

Radiation source: SEALED TUBE

Graphite monochromator

ω - 2θ scan

Absorption correction: multi-scan
(SADABS; Bruker, 2007)

$T_{\min} = 0.962$, $T_{\max} = 0.979$

7696 measured reflections

2975 independent reflections

2322 reflections with $I > 2\Sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 28.2^\circ$, $\theta_{\min} = 1.5^\circ$

$h = -7 \rightarrow 6$

$k = -10 \rightarrow 11$

$l = -34 \rightarrow 32$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.075$

$wR(F^2) = 0.148$

$S = 1.18$

2975 reflections

173 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

Weighting scheme based on measured s.u.'s

$(\Delta/\sigma)_{\max} = 0.006$

$\Delta\rho_{\max} = 0.23$ e Å⁻³

$\Delta\rho_{\min} = -0.24$ e Å⁻³

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
F14	0.0103 (6)	0.1908 (3)	0.41628 (9)	0.0777 (11)
O7	-0.3466 (5)	0.3868 (3)	0.20473 (10)	0.0501 (9)
O16	0.0782 (6)	0.1173 (4)	0.04855 (10)	0.0675 (11)
O19	0.3634 (6)	0.0024 (4)	0.09592 (11)	0.0665 (11)
N1	-0.0226 (5)	0.2174 (3)	0.21258 (11)	0.0380 (9)
N6	0.3131 (6)	0.0484 (3)	0.19821 (11)	0.0449 (10)
C2	-0.1947 (7)	0.3016 (4)	0.18607 (14)	0.0402 (11)
C3	-0.1510 (8)	0.2676 (4)	0.13223 (14)	0.0457 (12)
C4	0.0711 (7)	0.1663 (4)	0.13244 (13)	0.0403 (11)
C5	0.1342 (6)	0.1388 (4)	0.18000 (13)	0.0351 (11)
C8	-0.0114 (6)	0.2105 (4)	0.26584 (12)	0.0345 (11)
C9	0.1786 (7)	0.2794 (4)	0.29063 (14)	0.0420 (12)
C10	0.1843 (8)	0.2732 (5)	0.34181 (15)	0.0503 (12)
C11	0.0017 (8)	0.1985 (5)	0.36617 (14)	0.0490 (14)
C12	-0.1879 (8)	0.1282 (5)	0.34218 (15)	0.0527 (16)
C13	-0.1941 (7)	0.1362 (4)	0.29129 (14)	0.0437 (12)
C15	0.1869 (8)	0.0873 (5)	0.09193 (14)	0.0473 (12)
C17	0.1672 (12)	0.0330 (8)	0.00528 (17)	0.094 (2)
C18	-0.0234 (14)	-0.0020 (10)	-0.0268 (2)	0.134 (4)
H9	0.30124	0.32939	0.27321	0.0506*
H10	0.31042	0.31912	0.35929	0.0606*
H12	-0.30851	0.07676	0.35975	0.0630*
H13	-0.32196	0.09126	0.27406	0.0526*
H31	-0.12308	0.36342	0.11386	0.0551*
H32	-0.28713	0.21277	0.11777	0.0551*
H61	0.40656	-0.00181	0.17837	0.0539*
H62	0.33375	0.04110	0.22967	0.0539*
H171	0.28599	0.09643	-0.01185	0.1126*
H172	0.24516	-0.06313	0.01573	0.1126*
H181	0.03741	-0.05787	-0.05497	0.2012*
H182	-0.09846	0.09335	-0.03758	0.2012*
H183	-0.14019	-0.06545	-0.00986	0.2012*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F14	0.087 (2)	0.109 (2)	0.0371 (14)	0.006 (2)	-0.0004 (14)	0.0091 (13)
O7	0.0503 (16)	0.0487 (14)	0.0512 (16)	0.0128 (15)	-0.0068 (14)	-0.0092 (12)
O16	0.071 (2)	0.098 (2)	0.0334 (15)	0.011 (2)	-0.0043 (14)	-0.0106 (16)
O19	0.064 (2)	0.084 (2)	0.0516 (18)	0.017 (2)	0.0054 (15)	-0.0114 (16)

N1	0.0386 (17)	0.0400 (15)	0.0355 (17)	0.0025 (15)	-0.0067 (14)	0.0008 (13)
N6	0.0452 (19)	0.0525 (18)	0.0371 (17)	0.0057 (17)	0.0003 (15)	-0.0050 (14)
C2	0.046 (2)	0.0337 (18)	0.041 (2)	0.0002 (19)	-0.0057 (19)	-0.0048 (16)
C3	0.050 (2)	0.043 (2)	0.044 (2)	-0.001 (2)	-0.012 (2)	-0.0030 (17)
C4	0.042 (2)	0.0419 (19)	0.037 (2)	0.0004 (17)	-0.0040 (17)	-0.0021 (17)
C5	0.0337 (19)	0.0340 (17)	0.0377 (19)	-0.0045 (16)	-0.0009 (16)	-0.0005 (15)
C8	0.034 (2)	0.0346 (17)	0.0349 (19)	0.0072 (17)	0.0009 (16)	-0.0007 (14)
C9	0.042 (2)	0.043 (2)	0.041 (2)	-0.008 (2)	-0.0008 (18)	0.0053 (16)
C10	0.045 (2)	0.057 (2)	0.049 (2)	0.000 (2)	-0.012 (2)	-0.0007 (19)
C11	0.057 (3)	0.059 (2)	0.031 (2)	0.010 (2)	0.000 (2)	0.0080 (18)
C12	0.045 (2)	0.062 (3)	0.051 (3)	-0.001 (2)	0.011 (2)	0.011 (2)
C13	0.036 (2)	0.045 (2)	0.050 (2)	-0.0025 (19)	-0.0008 (18)	-0.0012 (18)
C15	0.048 (2)	0.052 (2)	0.042 (2)	-0.006 (2)	-0.0012 (19)	-0.0025 (18)
C17	0.091 (4)	0.146 (5)	0.045 (3)	0.017 (5)	0.002 (3)	-0.025 (3)
C18	0.108 (6)	0.205 (8)	0.090 (4)	0.009 (6)	-0.017 (4)	-0.078 (5)

Geometric parameters (Å, °)

F14—C11	1.357 (5)	C9—C10	1.385 (6)
O7—C2	1.221 (5)	C10—C11	1.365 (6)
O16—C15	1.343 (5)	C11—C12	1.372 (6)
O16—C17	1.459 (6)	C12—C13	1.378 (6)
O19—C15	1.222 (6)	C17—C18	1.398 (9)
N1—C2	1.393 (5)	C3—H31	0.9700
N1—C5	1.407 (4)	C3—H32	0.9700
N1—C8	1.442 (4)	C9—H9	0.9300
N6—C5	1.349 (5)	C10—H10	0.9300
C2—C3	1.503 (5)	C12—H12	0.9300
C3—C4	1.504 (6)	C13—H13	0.9300
C4—C5	1.353 (5)	C17—H171	0.9700
C4—C15	1.437 (5)	C17—H172	0.9700
N6—H61	0.8600	C18—H181	0.9600
N6—H62	0.8600	C18—H182	0.9600
C8—C13	1.378 (5)	C18—H183	0.9600
C8—C9	1.379 (5)		
C15—O16—C17	117.0 (4)	O16—C15—C4	112.1 (4)
C2—N1—C5	110.3 (3)	O19—C15—C4	124.7 (4)
C2—N1—C8	124.4 (3)	O16—C17—C18	110.4 (5)
C5—N1—C8	125.4 (3)	C2—C3—H31	111.00
O7—C2—N1	124.5 (3)	C2—C3—H32	111.00
O7—C2—C3	128.7 (4)	C4—C3—H31	111.00
N1—C2—C3	106.7 (3)	C4—C3—H32	111.00
C2—C3—C4	103.8 (3)	H31—C3—H32	109.00
C3—C4—C5	108.4 (3)	C8—C9—H9	120.00
C3—C4—C15	129.2 (3)	C10—C9—H9	120.00
C5—C4—C15	121.8 (3)	C9—C10—H10	121.00
N1—C5—N6	119.9 (3)	C11—C10—H10	121.00

N1—C5—C4	110.6 (3)	C11—C12—H12	121.00
N6—C5—C4	129.5 (3)	C13—C12—H12	121.00
C5—N6—H62	120.00	C8—C13—H13	120.00
H61—N6—H62	120.00	C12—C13—H13	120.00
C5—N6—H61	120.00	O16—C17—H171	110.00
C9—C8—C13	120.9 (3)	O16—C17—H172	110.00
N1—C8—C13	119.1 (3)	C18—C17—H171	110.00
N1—C8—C9	120.0 (3)	C18—C17—H172	110.00
C8—C9—C10	119.1 (4)	H171—C17—H172	108.00
C9—C10—C11	118.9 (4)	C17—C18—H181	109.00
F14—C11—C10	118.6 (4)	C17—C18—H182	109.00
F14—C11—C12	118.5 (4)	C17—C18—H183	109.00
C10—C11—C12	122.9 (4)	H181—C18—H182	109.00
C11—C12—C13	118.0 (4)	H181—C18—H183	109.00
C8—C13—C12	120.2 (4)	H182—C18—H183	109.00
O16—C15—O19	123.3 (4)		
C17—O16—C15—O19	5.0 (7)	C3—C4—C5—N6	176.4 (3)
C17—O16—C15—C4	-174.9 (4)	C15—C4—C5—N1	-173.6 (3)
C15—O16—C17—C18	144.6 (5)	C15—C4—C5—N6	4.7 (6)
C5—N1—C2—O7	-176.3 (3)	C3—C4—C15—O16	2.6 (6)
C8—N1—C2—O7	4.7 (5)	C3—C4—C5—N1	-1.9 (4)
C5—N1—C2—C3	2.9 (4)	C3—C4—C15—O19	-177.3 (4)
C5—N1—C8—C9	69.1 (4)	C5—C4—C15—O16	172.5 (4)
C2—N1—C8—C13	67.1 (4)	C5—C4—C15—O19	-7.4 (7)
C5—N1—C8—C13	-111.7 (4)	N1—C8—C9—C10	179.2 (3)
C2—N1—C5—N6	-179.2 (3)	C13—C8—C9—C10	0.0 (5)
C8—N1—C5—N6	-0.2 (5)	N1—C8—C13—C12	-179.9 (3)
C2—N1—C5—C4	-0.7 (4)	C9—C8—C13—C12	-0.7 (5)
C8—N1—C5—C4	178.3 (3)	C8—C9—C10—C11	0.2 (6)
C2—N1—C8—C9	-112.1 (4)	C9—C10—C11—C12	0.3 (7)
C8—N1—C2—C3	-176.1 (3)	C9—C10—C11—F14	179.0 (4)
O7—C2—C3—C4	175.4 (4)	F14—C11—C12—C13	-179.7 (4)
N1—C2—C3—C4	-3.8 (4)	C10—C11—C12—C13	-1.0 (7)
C2—C3—C4—C5	3.5 (4)	C11—C12—C13—C8	1.2 (6)
C2—C3—C4—C15	174.4 (4)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N6—H61...O19	0.86	2.2400	2.806 (4)	123
N6—H62...O7 ⁱ	0.86	2.2100	2.970 (4)	147
C13—H13...O7 ⁱⁱ	0.93	2.6000	3.320 (5)	135
C17—H172...O19	0.97	2.3300	2.692 (6)	101

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