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(*E*)-Ethyl 4-chloro-3-[2-(2-fluorophenyl)hydrazono]butanoate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.099
Data-to-parameter ratio = 18.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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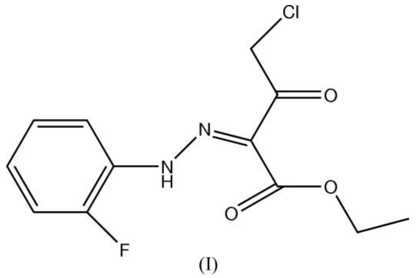
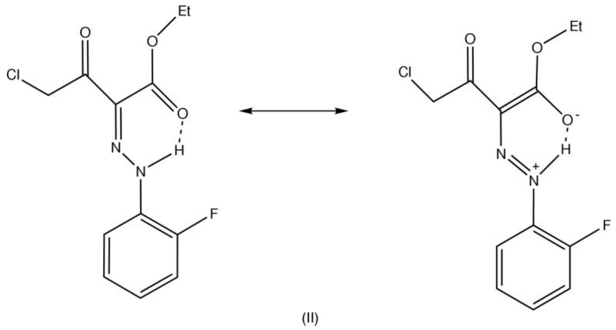
The title compound, $C_{12}H_{12}ClFN_2O_3$, adopts a keto–hydrazo tautomeric form stabilized by an intramolecular N—H···O hydrogen bond. The whole molecule is roughly planar, the largest deviation from the mean plane being 0.328 (3) Å for the terminal methyl C atom of the ethyl side chain.

Comment

The chemistry of hydrazones has been intensively investigated in recent years, owing to their coordination capability, pharmacological activity and antibacterial and antifungal properties, and their use in analytical chemistry as highly selective extractants (Domiano *et al.*, 1984; Sakamoto *et al.*, 1993; Li *et al.*, 1988). As part of our project studying the crystal structures of a series of phenylhydrazones and their stereochemistry, the crystal structure of the title compound, (I), has been determined. The chemical background of (I) was described in a previous paper (Odabaşoğlu *et al.*, 2005*a*). We have previously reported the structures of ethyl 4-chloro-2-[(2-nitrophenyl)hydrazono]-3-oxobutyrate, (II) (Odabaşoğlu *et al.*, 2005*a*), ethyl 4-chloro-2-[(4-nitrophenyl)hydrazono]-3-oxobutyrate, (III) (Odabaşoğlu *et al.*, 2005*b*) and ethyl 4-chloro-3-oxo-2-(phenylhydrazono)butyrate, (IV) (Alpaslan *et al.*, 2005).



(I)



(II)

The bond lengths and angles in (I) show normal values and are comparable with those observed for (II), (III) and (IV).

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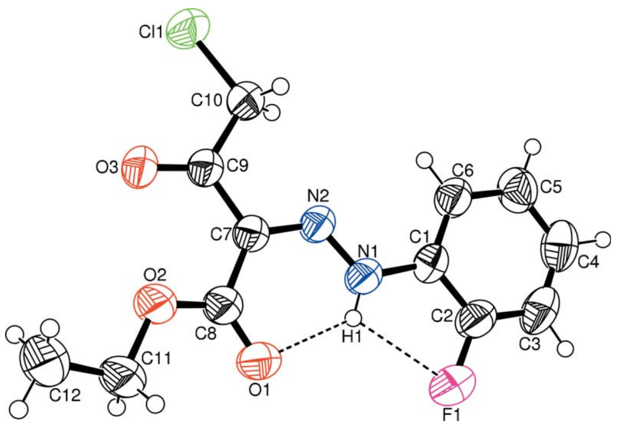

Figure 1
A view of the molecule of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probalitity level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate the intramolecular hydrogen bonds.

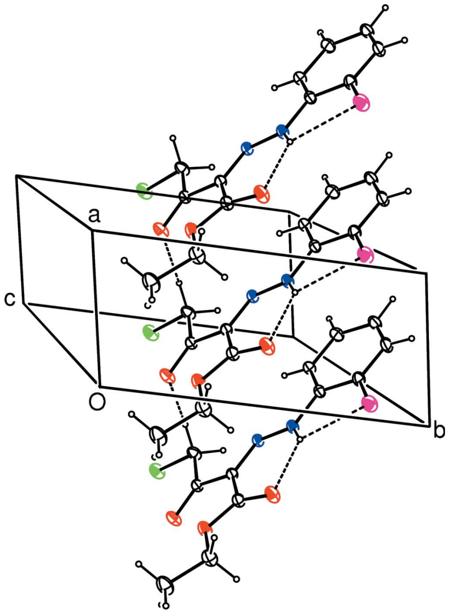

Figure 2
A packing diagram for the title compound, showing the hydrogen-bonding scheme (dashed lines).

The molecular structure and atom-labelling scheme are shown in Fig. 1. The whole molecule is roughly planar, the largest deviation from the mean plane being 0.328 (3) Å for atom C12.

There is a moderately strong intramolecular N1—H1···O1 hydrogen bond, which appears to be a common feature for similar systems [N—H···O 1.99 (2) Å in ethyl 4-chloro-3-oxo-2-(phenlyhydrazono)butyrate (Alpaslan *et al.*, 2005); N—H···O 1.97 Å in 4-chloro-2-(4-oxopent-2-en-2-ylamino)-phenol (Arıcı *et al.*, 1999)]. Besides this, there are an intramolecular N—H···F hydrogen bond and an intermolecular C—H···O interaction.

The N1—N2 single bond distance of 1.306 (2) Å is shorter than that observed in 1,2-bis-[1-(3-pyridyl)3-methyltriazen-3-yl]ethane [1.326 (3) Å; Vaughan *et al.*, 2004]. This shortening in the hydrazone group is consistent with the resonance structure shown in the second scheme, which gives the N1—N2 bond some double-bond character.

Experimental

A mixture of *o*-fluoroaniline (10 mmol), water (50 ml) and concentrated hydrochloric acid (30 mmmol) was heated with stirring until a clear solution was obtained. This solution was cooled to 273–278 mK and a solution of sodium nitrite (14 mmmol) in water was added dropwise while the temperature was maintained below 278 mK. The resulting mixture was stirred for 30 mmin in an ice bath. The pH was raised to 8–9 by adding dilute NaOH solution. Ethyl 4-chloroacetoacetate (10 mmmol) solution in ethanol was gradually added to a cooled solution of the *o*-fluorbenzenediazonium chloride, prepared as described above. The resulting mixture was stirred at 273–278 K for 60 min in an ice bath and the pH lowered to 5 with dilute HCl. The product was recrystallized from glacial acetic acid to obtain well shaped crystals of (I) (yield 93%; m.p. 413–414 K).

Crystal data

$C_{12}H_{12}ClFN_2O_3$
$M_r = 286.69$
Triclinic, $P\overline{1}$
$a = 4.3633$ (5) Å
$b = 9.2982$ (11) Å
$c = 16.7339$ (17) Å
$\alpha = 94.781$ (9)°
$\beta = 93.394$ (9)°
$\gamma = 100.822$ (9)°
$V = 662.57$ (13) Å^3
$Z = 2$
$D_x = 1.437$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9166 reflections
$\theta = 2.2$–27.9°
$\mu = 0.31$ mm^{-1}
$T = 296$ (2) K
Rod, red
0.42 × 0.25 × 0.15 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)
$T_{min} = 0.924$, $T_{max} = 0.968$
11451 measured reflections
3155 independent reflections
1687 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 27.9°$
$h = -5 \rightarrow 5$
$k = -12 \rightarrow 12$
$l = -21 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.099$
$S = 0.83$
3155 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.86	1.96	2.6067 (17)	132
N1—H1···F1	0.86	2.36	2.6743 (16)	102
C10—H10*B*···O3^{i}	0.97	2.54	3.383 (2)	145

Symmetry code: (i) $x + 1, y, z$.

All H atoms were found in difference Fourier synthesis, but they were introduced in calculated positions and treated as riding on their parent atoms, with C—H = 0.93–0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ [$1.5U_{eq}$(methyl C)], and with N—H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(N)$.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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