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Ethyl 2-(3,5-difluorophenyl)quinoline-4-carboxylate: a second triclinic polymorph

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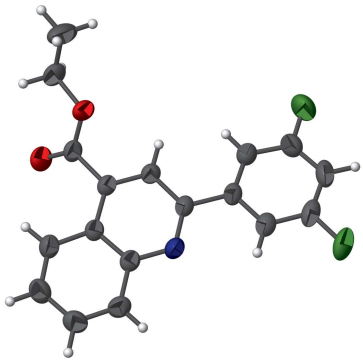
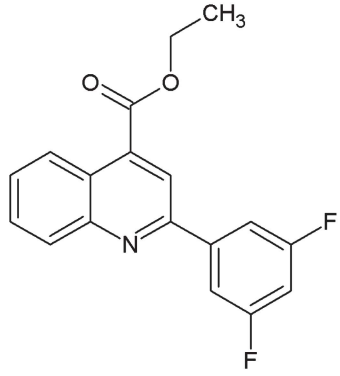
The title compound, $C_{18}H_{13}F_2NO_2$, is a polymorph of the structure reported by Sunitha *et al.* [*Acta Cryst.* (2015), E**71**, o341–o342]. Both compounds crystallize in the triclinic space group $P\overline{1}$. The principal difference between the two polymorphs lies in the orientation of the carboxylate substituents with respect to the planes of the quinoline ring systems. In the crystal, the packing features C—H···O hydrogen bonds together with short C—F···π and π–π interactions.

3D view



Chemical scheme



Structure description

The title compound (I), Fig. 1, which crystallizes in the triclinic space group $P\overline{1}$, is a polymorph of the structure (II) reported by Sunitha *et al.* (2015), also in $P\overline{1}$. In both polymorphs, the difluorophenyl rings lie close to the planes of the quinoline ring system with dihedral angles of 10.85 (10)° for (I) and 7.65 (7)° for (II). In contrast however, the carboxylate substituent in (I) projects away from one face of the quinoline ring system, with the angle between the best fit plane through O12/C10–C15 inclined to the quinoline plane by 42.17 (9)°, while for (II) the carboxylate lies close to the quinoline plane, with a corresponding dihedral angle of *ca* 5.87 (8)°. The torsion angle between the carboxylate substituent and the quinoline ring system C10—C11—O13—C14 is 176.44 (16)°, indicating a + *anti-periplanar* conformation. This is opposite to the − *anti-periplanar* conformation found for (II) (Sunitha *et al.*, 2015). Intramolecular C2—H2···O12 and C21—H21···N7 hydrogen bonds, Table 1, also affect the overall molecular conformation. The structure of a closely related molecule, 2-(4-chlorophenyl)-6-methyl-4-(3-methylphenyl)quinoline was reported by Prabhuswamy *et al.* (2012).

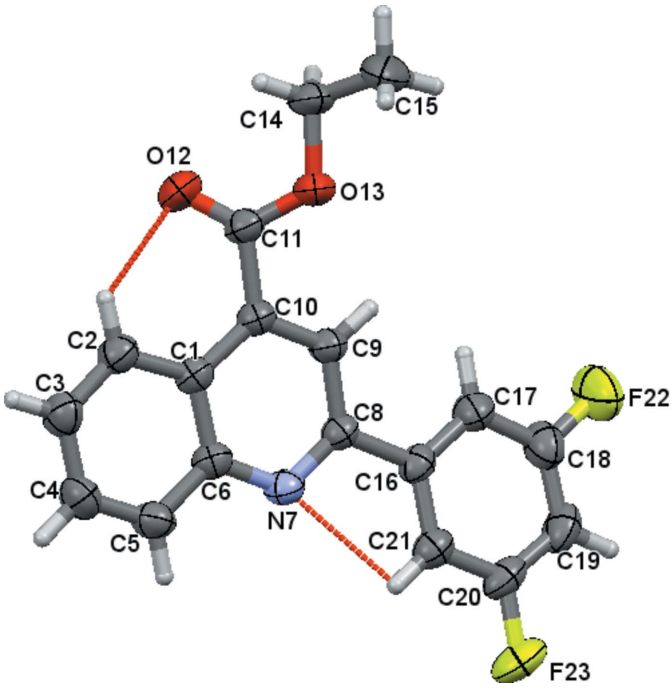


Figure 1
A view of the title molecule, with atom labelling. Displacement ellipsoids are drawn at the 50% probability level and intramolecular hydrogen bonds are shown as dashed lines.

In the crystal, molecules are linked through C19—H19···O12 hydrogen bonds into chains parallel to the *ab* diagonal, Table 1 and Fig. 2. A variety of π–π interactions are observed: $Cg1\cdots Cg1^{ii}$ = 3.8199 (11), $Cg1\cdots Cg2^{ii}$ = 3.6825 (12) and $Cg1\cdots Cg3^{iii}$ = 3.8722 (13) Å, *Cg*1, *Cg*2 and *Cg*3 are the centroids of the N7/C1/C6/C8–C10; C1–C6 and C16–C21 rings, respectively; symmetry codes: (ii) $-x, 2-y, 1-z$; (iii) $1-x, 2-y, 1-z$). C20—F23···$Cg1^{iii}$ [F···*Cg*1 = 3.6366 (17) Å] and C20—F23···$Cg3^{iv}$ [F···*Cg*3 = 3.3445 (18) Å; symmetry code: (iv) $1-x, 1-y, 1-z$] interactions also occur.

Synthesis and crystallization

Synthesis was performed using a literature method (Sunitha *et al.*, 2015). Recrystallization was carried out using the slow evaporation technique from ethanol solution.

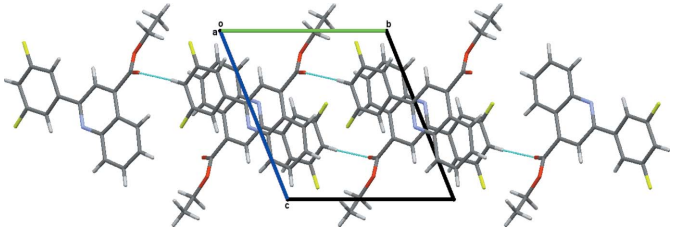


Figure 2
A view along the *a* axis of the crystal packing of the title compound. Hydrogen bonds are drawn as dashed lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O12	0.93	2.41	2.986 (2)	120
C21—H21···N7	0.93	2.47	2.778 (3)	100
C19—H19···O12^{i}	0.93	2.47	3.399 (3)	175

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{13}F_2NO_2$
M_r	313.29
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	293
a, *b*, *c* (Å)	8.9998 (8), 9.0314 (6), 10.2747 (5)
α, β, γ (°)	67.15 (2), 72.45 (3), 82.91 (3)
V (Å^3)	733.76 (18)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.11
Crystal size (mm)	0.6 × 0.5 × 0.3
Data collection	
Diffractometer	Rigaku Saturn724+
Absorption correction	Multi-scan (*NUMABS*; Rigaku 1999)
T_{min}, T_{max}	0.936, 0.968
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4288, 3269, 2198
R_{int}	0.038
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.058, 0.172, 1.05
No. of reflections	3269
No. of parameters	209
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.20

Computer programs: *CrystalClear SM-Expert* (Rigaku, 2011), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_{18}H_{13}F_2NO_2$
M_r = 313.29
Triclinic, $P\overline{1}$
a = 8.9998 (8) Å
b = 9.0314 (6) Å
c = 10.2747 (5) Å
α = 67.15 (2)°
β = 72.45 (3)°
γ = 82.91 (3)°
V = 733.76 (18) Å^3
Z = 2
$F(000)$ = 324
D_x = 1.418 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3269 reflections
θ = 27.5–3.1°
μ = 0.11 mm^{-1}
T = 293 K
Block, colourless
0.6 × 0.5 × 0.3 mm

Data collection

Rigaku Saturn724+ diffractometer
Detector resolution: 28.5714 pixels mm^{-1}
profile data from ω–scans
Absorption correction: multi-scan (*NUMABS*; Rigaku 1999)
T_{min} = 0.936, T_{max} = 0.968
4288 measured reflections
3269 independent reflections
2198 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 27.5°, θ_{min} = 3.1°
h = −11→11
k = −11→8
l = −13→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.172
S = 1.05
3269 reflections
209 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0867P)^2 + 0.0798P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
F22	0.6825 (2)	0.7904 (2)	0.07067 (16)	0.1001 (6)
F23	0.67056 (16)	0.53755 (15)	0.56697 (16)	0.0718 (4)
O12	−0.01987 (17)	1.4064 (2)	0.24797 (16)	0.0649 (5)
O13	0.23514 (16)	1.42864 (17)	0.13543 (14)	0.0531 (4)
N7	0.24653 (18)	0.94165 (18)	0.57154 (16)	0.0421 (4)
C1	0.0774 (2)	1.1781 (2)	0.51318 (19)	0.0376 (4)
C2	−0.0454 (2)	1.2713 (2)	0.5691 (2)	0.0480 (5)
H2	−0.0801	1.3639	0.5047	0.058*
C3	−0.1123 (3)	1.2258 (3)	0.7167 (2)	0.0539 (5)
H3	−0.1929	1.2874	0.7519	0.065*
C4	−0.0618 (3)	1.0881 (3)	0.8155 (2)	0.0555 (5)
H4	−0.1086	1.0588	0.9159	0.067*
C5	0.0558 (2)	0.9962 (2)	0.7659 (2)	0.0503 (5)
H5	0.0882	0.9044	0.8329	0.060*
C6	0.1290 (2)	1.0385 (2)	0.61443 (19)	0.0401 (4)
C8	0.3163 (2)	0.9798 (2)	0.43039 (19)	0.0388 (4)
C9	0.2746 (2)	1.1196 (2)	0.3221 (2)	0.0405 (4)
H9	0.3281	1.1449	0.2234	0.049*
C10	0.1566 (2)	1.2166 (2)	0.36229 (19)	0.0383 (4)
C11	0.1116 (2)	1.3604 (2)	0.2447 (2)	0.0426 (4)
C14	0.2048 (3)	1.5635 (3)	0.0110 (2)	0.0608 (6)
H14A	0.1244	1.6326	0.0450	0.073*
H14B	0.1698	1.5253	−0.0509	0.073*
C15	0.3529 (3)	1.6536 (4)	−0.0731 (3)	0.0974 (11)
H15A	0.3348	1.7481	−0.1521	0.146*
H15B	0.4292	1.5865	−0.1125	0.146*
H15C	0.3903	1.6842	−0.0090	0.146*
C16	0.4429 (2)	0.8708 (2)	0.3884 (2)	0.0408 (4)
C17	0.5062 (3)	0.8827 (2)	0.2435 (2)	0.0534 (5)
H17	0.4699	0.9601	0.1686	0.064*
C18	0.6236 (3)	0.7778 (3)	0.2130 (3)	0.0606 (6)
C19	0.6821 (2)	0.6602 (3)	0.3172 (3)	0.0588 (6)
H19	0.7611	0.5905	0.2935	0.071*
C20	0.6169 (2)	0.6520 (2)	0.4584 (3)	0.0509 (5)
C21	0.4994 (2)	0.7514 (2)	0.4975 (2)	0.0453 (5)
H21	0.4578	0.7395	0.5955	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F22	0.1142 (14)	0.0950 (12)	0.0644 (9)	0.0349 (10)	0.0037 (9)	−0.0335 (8)
F23	0.0743 (9)	0.0543 (8)	0.0933 (10)	0.0268 (7)	−0.0468 (8)	−0.0246 (7)
O12	0.0491 (9)	0.0713 (11)	0.0610 (10)	0.0189 (8)	−0.0218 (7)	−0.0113 (8)
O13	0.0508 (8)	0.0528 (9)	0.0406 (7)	0.0100 (6)	−0.0154 (6)	−0.0027 (6)
N7	0.0473 (9)	0.0345 (8)	0.0422 (8)	0.0038 (7)	−0.0157 (7)	−0.0108 (6)

C1	0.0384 (9)	0.0362 (9)	0.0413 (9)	0.0023 (7)	−0.0148 (7)	−0.0157 (7)
C2	0.0486 (11)	0.0452 (11)	0.0513 (11)	0.0086 (9)	−0.0183 (9)	−0.0185 (9)
C3	0.0526 (12)	0.0622 (13)	0.0511 (11)	0.0097 (10)	−0.0134 (9)	−0.0291 (10)
C4	0.0596 (13)	0.0638 (14)	0.0414 (11)	0.0027 (11)	−0.0096 (9)	−0.0220 (10)
C5	0.0609 (13)	0.0481 (12)	0.0389 (10)	0.0031 (10)	−0.0164 (9)	−0.0121 (8)
C6	0.0433 (10)	0.0377 (9)	0.0419 (10)	0.0013 (8)	−0.0162 (8)	−0.0146 (8)
C8	0.0400 (10)	0.0338 (9)	0.0426 (10)	0.0035 (7)	−0.0139 (8)	−0.0135 (7)
C9	0.0433 (10)	0.0388 (10)	0.0378 (9)	0.0040 (8)	−0.0136 (8)	−0.0120 (8)
C10	0.0406 (10)	0.0347 (9)	0.0402 (9)	0.0028 (7)	−0.0160 (7)	−0.0120 (7)
C11	0.0477 (11)	0.0410 (10)	0.0410 (10)	0.0097 (8)	−0.0185 (8)	−0.0156 (8)
C14	0.0688 (15)	0.0597 (14)	0.0434 (11)	0.0182 (11)	−0.0256 (10)	−0.0059 (10)
C15	0.0709 (18)	0.095 (2)	0.0630 (16)	0.0102 (16)	−0.0056 (13)	0.0247 (15)
C16	0.0382 (9)	0.0333 (9)	0.0508 (10)	0.0025 (7)	−0.0128 (8)	−0.0159 (8)
C17	0.0556 (12)	0.0439 (11)	0.0512 (12)	0.0080 (9)	−0.0117 (9)	−0.0124 (9)
C18	0.0615 (14)	0.0524 (13)	0.0585 (13)	0.0042 (11)	−0.0012 (10)	−0.0235 (10)
C19	0.0447 (12)	0.0472 (12)	0.0803 (16)	0.0114 (9)	−0.0109 (11)	−0.0278 (11)
C20	0.0447 (11)	0.0358 (10)	0.0756 (14)	0.0069 (8)	−0.0284 (10)	−0.0175 (9)
C21	0.0456 (11)	0.0398 (10)	0.0535 (11)	0.0032 (8)	−0.0189 (9)	−0.0176 (9)

Geometric parameters (Å, º)

F22—C18	1.360 (3)	C8—C16	1.487 (2)
F23—C20	1.361 (2)	C9—H9	0.9300
O12—C11	1.200 (2)	C9—C10	1.361 (2)
O13—C11	1.325 (2)	C10—C11	1.503 (2)
O13—C14	1.453 (2)	C14—H14A	0.9700
N7—C6	1.367 (2)	C14—H14B	0.9700
N7—C8	1.316 (2)	C14—C15	1.487 (4)
C1—C2	1.422 (3)	C15—H15A	0.9600
C1—C6	1.420 (2)	C15—H15B	0.9600
C1—C10	1.417 (3)	C15—H15C	0.9600
C2—H2	0.9300	C16—C17	1.390 (3)
C2—C3	1.362 (3)	C16—C21	1.395 (3)
C3—H3	0.9300	C17—H17	0.9300
C3—C4	1.394 (3)	C17—C18	1.377 (3)
C4—H4	0.9300	C18—C19	1.368 (3)
C4—C5	1.362 (3)	C19—H19	0.9300
C5—H5	0.9300	C19—C20	1.367 (3)
C5—C6	1.408 (3)	C20—C21	1.370 (3)
C8—C9	1.420 (2)	C21—H21	0.9300
C11—O13—C14	116.37 (15)	O13—C11—C10	111.54 (15)
C8—N7—C6	118.80 (15)	O13—C14—H14A	110.2
C6—C1—C2	118.52 (17)	O13—C14—H14B	110.2
C10—C1—C2	124.76 (16)	O13—C14—C15	107.47 (18)
C10—C1—C6	116.69 (16)	H14A—C14—H14B	108.5
C1—C2—H2	119.8	C15—C14—H14A	110.2
C3—C2—C1	120.33 (18)	C15—C14—H14B	110.2

C3—C2—H2	119.8	C14—C15—H15A	109.5
C2—C3—H3	119.5	C14—C15—H15B	109.5
C2—C3—C4	120.9 (2)	C14—C15—H15C	109.5
C4—C3—H3	119.5	H15A—C15—H15B	109.5
C3—C4—H4	119.8	H15A—C15—H15C	109.5
C5—C4—C3	120.36 (19)	H15B—C15—H15C	109.5
C5—C4—H4	119.8	C17—C16—C8	122.06 (17)
C4—C5—H5	119.6	C17—C16—C21	118.63 (18)
C4—C5—C6	120.87 (18)	C21—C16—C8	119.30 (17)
C6—C5—H5	119.6	C16—C17—H17	120.6
N7—C6—C1	122.89 (16)	C18—C17—C16	118.79 (19)
N7—C6—C5	118.10 (16)	C18—C17—H17	120.6
C5—C6—C1	119.01 (18)	F22—C18—C17	117.8 (2)
N7—C8—C9	121.95 (17)	F22—C18—C19	118.2 (2)
N7—C8—C16	117.07 (16)	C19—C18—C17	124.0 (2)
C9—C8—C16	120.97 (16)	C18—C19—H19	122.2
C8—C9—H9	119.9	C20—C19—C18	115.57 (19)
C10—C9—C8	120.18 (17)	C20—C19—H19	122.2
C10—C9—H9	119.9	F23—C20—C19	118.31 (19)
C1—C10—C11	121.64 (16)	F23—C20—C21	117.9 (2)
C9—C10—C1	119.46 (16)	C19—C20—C21	123.82 (19)
C9—C10—C11	118.89 (16)	C16—C21—H21	120.4
O12—C11—O13	124.14 (17)	C20—C21—C16	119.18 (19)
O12—C11—C10	124.31 (18)	C20—C21—H21	120.4

F22—C18—C19—C20	−179.1 (2)	C8—C9—C10—C1	0.9 (3)
F23—C20—C21—C16	179.44 (16)	C8—C9—C10—C11	−177.89 (16)
N7—C8—C9—C10	−1.8 (3)	C8—C16—C17—C18	179.82 (19)
N7—C8—C16—C17	168.68 (18)	C8—C16—C21—C20	−179.52 (17)
N7—C8—C16—C21	−10.6 (3)	C9—C8—C16—C17	−12.0 (3)
C1—C2—C3—C4	0.3 (3)	C9—C8—C16—C21	168.72 (16)
C1—C10—C11—O12	−37.0 (3)	C9—C10—C11—O12	141.7 (2)
C1—C10—C11—O13	144.05 (17)	C9—C10—C11—O13	−37.2 (2)
C2—C1—C6—N7	−179.66 (16)	C10—C1—C2—C3	−178.75 (19)
C2—C1—C6—C5	0.8 (3)	C10—C1—C6—N7	−1.4 (3)
C2—C1—C10—C9	178.70 (17)	C10—C1—C6—C5	179.03 (17)
C2—C1—C10—C11	−2.5 (3)	C11—O13—C14—C15	162.0 (2)
C2—C3—C4—C5	−0.1 (3)	C14—O13—C11—O12	−2.5 (3)
C3—C4—C5—C6	0.3 (3)	C14—O13—C11—C10	176.44 (16)
C4—C5—C6—N7	179.84 (18)	C16—C8—C9—C10	178.90 (16)
C4—C5—C6—C1	−0.6 (3)	C16—C17—C18—F22	179.2 (2)
C6—N7—C8—C9	1.0 (3)	C16—C17—C18—C19	0.5 (4)
C6—N7—C8—C16	−179.68 (15)	C17—C16—C21—C20	1.2 (3)
C6—C1—C2—C3	−0.7 (3)	C17—C18—C19—C20	−0.4 (4)
C6—C1—C10—C9	0.6 (3)	C18—C19—C20—F23	−179.87 (19)
C6—C1—C10—C11	179.39 (16)	C18—C19—C20—C21	0.7 (3)
C8—N7—C6—C1	0.6 (3)	C19—C20—C21—C16	−1.1 (3)
C8—N7—C6—C5	−179.84 (17)	C21—C16—C17—C18	−0.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O12	0.93	2.41	2.986 (2)	120
C21—H21···N7	0.93	2.47	2.778 (3)	100
C19—H19···O12^{i}	0.93	2.47	3.399 (3)	175

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