

Ethyl 2-phenyl-5-trifluoromethyl-1,3-thiazole-4-carboxylate

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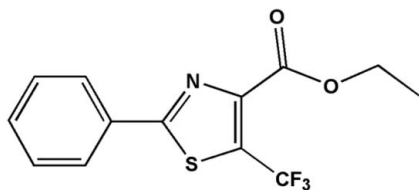
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.056; wR factor = 0.142; data-to-parameter ratio = 13.0.

In the title compound, $\text{C}_{13}\text{H}_{10}\text{F}_3\text{NO}_2\text{S}$, the dihedral angle between the thiazole and phenyl rings is $5.15(1)^\circ$. No intermolecular hydrogen bonding is observed in the crystal structure.

Related literature

For general background, see: Sasse *et al.* (2002); Campeau *et al.* (2008); Zifcsak & Hlasta (2004); Rynbrandt *et al.* (1981). For a related structure, see: Kennedy *et al.* (2004).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{10}\text{F}_3\text{NO}_2\text{S}$
 $M_r = 301.28$

Monoclinic, $P2_1/c$
 $a = 8.930(3)$ Å

$b = 21.232(6)$ Å
 $c = 7.574(2)$ Å
 $\beta = 110.861(4)^\circ$
 $V = 1342.0(7)$ Å³
 $Z = 4$

Mo $K\alpha$ radiation
 $\mu = 0.28$ mm⁻¹
 $T = 296(2)$ K
 $0.30 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.922$, $T_{\max} = 0.973$

6891 measured reflections
2367 independent reflections
1417 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.142$
 $S = 1.01$
2367 reflections

182 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2454).

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supplementary materials

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Ethyl 2-phenyl-5-trifluoromethyl-1,3-thiazole-4-carboxylate

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Comment

1,3-Thiazole derivatives have attracted considerable attention because of various biological activities (Sasse *et al.*, 2002) and have broad applications in the materials science (Campeau *et al.*, 2008). Thiazole can be used as a core for developing pharmaceutically important molecules (Zifcisk & Hlasta, 2004). Trifluoromethyl substituted thiazole may be the most promising skeleton in medicinal chemistry (Rynbrandt *et al.*, 1981). The title compound, multiple substitute 1,3-thiazol with trifluoromethyl group at 5-position, has been obtained unexpectedly in the laboratory during trying to prepare 3-chloro-2-dibenzylamino-4,4,4-trifluoro-butyrac acid ethyl ester by a reaction of 2-dibenzylamino-4,4,4-trifluoro-3-hydroxy-butyrac acid ethyl ester with thionyl chloride. We present here the crystal structure of the title compound.

The molecular structure is shown in Fig. 1. The bond lengths in the thiazole moiety agree with those found in methyl 2-amino-5-isopropyl-1,3-thiazole-4-carboxylate (Kennedy *et al.*, 2004). The thiazole ring makes a dihedral angle of 5.15 (1)° with phenyl ring, showing the approximately coplanar molecular structure except for trifluoromethyl and ethoxy group. No intermolecular hydrogen bonding is observed in the crystal structure.

Experimental

A solution of 2-dibenzylamino-4,4,4-trifluoro-3-hydroxy-butyrac acid ethyl ester (0.2 mmol) in 10 ml thionyl chloride was refluxed for a period of half an hour till the complete consumption of raw material. Excess thionyl chloride was evaporated, the residue was diluted with anhydrous ethanol (4 ml), then concentrated by rotary evaporator. The crude product was re-crystallized from ethanol (95%) and colorless needle-type crystals of (I) were obtained.

Refinement

All the H atoms were placed in geometrically idealized positions and constrained to ride their parent atoms, with C—H = 0.93 - 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl and $1.2U_{\text{eq}}(\text{C})$ for others.

Figures

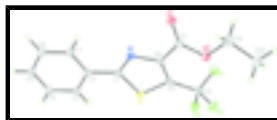


Fig. 1. View of the title compound (I), shown the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented by circles of arbitrary radii.

Ethyl 2-phenyl-5-trifluoromethyl-1,3-thiazole-4-carboxylate

Crystal data

C₁₃H₁₀F₃NO₂S

$F_{000} = 616$

supplementary materials

$M_r = 301.28$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.930$ (3) Å

$b = 21.232$ (6) Å

$c = 7.574$ (2) Å

$\beta = 110.861$ (4)°

$V = 1342.0$ (7) Å³

$Z = 4$

$D_x = 1.491$ Mg m⁻³

Melting point: 320 K

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1005 reflections

$\theta = 2.5$ – 19.0 °

$\mu = 0.28$ mm⁻¹

$T = 296$ (2) K

Needle, colorless

$0.30 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296$ (2) K

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.922$, $T_{\max} = 0.973$

6891 measured reflections

2367 independent reflections

1417 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 25.1$ °

$\theta_{\min} = 2.4$ °

$h = -10 \rightarrow 10$

$k = -25 \rightarrow 19$

$l = -8 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.142$

$S = 1.01$

2367 reflections

182 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.22$ e Å⁻³

$\Delta\rho_{\min} = -0.19$ e Å⁻³

Extinction correction: none

Special details

Experimental. IR (KBr, cm⁻¹): 3061, 2980, 1737, 1633, 1513, 1461, 1290, 1210, 766, 689. ¹H NMR (CDCl₃, 500 MHz). δ /p.p.m.: 7.46–8.00 (m, 5H), 4.49 (q, $J = 7.0$ Hz, 2H), 1.44 (t, $J = 7.0$ Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz). δ /p.p.m.: 168.87, 160.27, 146.48, 131.77, 131.63, 129.24, 164.15 (q, ²J_{C–F} = 36.5 Hz, CF₃C–), 123.33 (q, ¹J_{C–F} = 269.3 Hz, –CF₃), 62.41, 13.98. ¹⁹F NMR (CDCl₃, 470 MHz, CFCl₃). δ /p.p.m.: -52.44 (s).

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.22302 (11)	0.67958 (4)	0.44789 (13)	0.0585 (3)
C1	0.1690 (4)	0.75511 (15)	0.3693 (5)	0.0504 (8)
C2	0.2697 (4)	0.80979 (15)	0.4545 (5)	0.0523 (8)
C3	0.4186 (4)	0.80233 (17)	0.5954 (5)	0.0615 (10)
H3	0.4559	0.7622	0.6376	0.074*
C4	0.5115 (4)	0.85408 (19)	0.6732 (5)	0.0681 (10)
H4	0.6116	0.8488	0.7671	0.082*
C5	0.4564 (5)	0.91329 (18)	0.6123 (6)	0.0720 (11)
H5	0.5192	0.9483	0.6646	0.086*
C6	0.3083 (5)	0.92108 (18)	0.4743 (6)	0.0741 (11)
H6	0.2708	0.9614	0.4343	0.089*
C7	0.2154 (4)	0.86972 (16)	0.3947 (5)	0.0642 (10)
H7	0.1156	0.8753	0.3004	0.077*
C8	-0.0328 (4)	0.70143 (16)	0.1739 (5)	0.0514 (8)
C9	0.0515 (4)	0.65213 (16)	0.2791 (5)	0.0517 (8)
C10	0.0138 (5)	0.58379 (17)	0.2771 (6)	0.0674 (10)
C11	-0.1837 (4)	0.69976 (18)	0.0062 (5)	0.0577 (9)
C12	-0.3482 (5)	0.63721 (19)	-0.2455 (6)	0.0857 (13)
H12A	-0.3442	0.6683	-0.3375	0.103*
H12B	-0.4455	0.6438	-0.2188	0.103*
C13	-0.3463 (7)	0.5732 (2)	-0.3197 (7)	0.133 (2)
H13A	-0.2565	0.5689	-0.3603	0.200*
H13B	-0.4438	0.5660	-0.4249	0.200*
H13C	-0.3375	0.5429	-0.2224	0.200*
F1	-0.1303 (3)	0.57367 (10)	0.2825 (4)	0.0973 (8)
F2	0.0198 (3)	0.55287 (10)	0.1294 (4)	0.0932 (8)
F3	0.1174 (3)	0.55518 (10)	0.4280 (4)	0.1071 (9)
N1	0.0337 (3)	0.75955 (12)	0.2277 (4)	0.0522 (7)
O1	-0.2677 (3)	0.74436 (12)	-0.0528 (4)	0.0791 (8)
O2	-0.2081 (3)	0.64335 (11)	-0.0726 (3)	0.0693 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0601 (6)	0.0546 (6)	0.0597 (6)	0.0055 (4)	0.0201 (5)	0.0032 (4)
C1	0.053 (2)	0.054 (2)	0.053 (2)	0.0023 (16)	0.0291 (19)	0.0011 (16)
C2	0.058 (2)	0.055 (2)	0.049 (2)	0.0007 (17)	0.0249 (18)	-0.0021 (17)

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C3	0.060 (2)	0.057 (2)	0.069 (3)	0.0017 (18)	0.024 (2)	0.0034 (18)
C4	0.058 (2)	0.075 (3)	0.066 (3)	-0.007 (2)	0.016 (2)	-0.003 (2)
C5	0.074 (3)	0.058 (3)	0.086 (3)	-0.010 (2)	0.030 (2)	-0.010 (2)
C6	0.073 (3)	0.057 (2)	0.089 (3)	0.004 (2)	0.024 (2)	-0.005 (2)
C7	0.063 (2)	0.054 (2)	0.070 (3)	0.0019 (18)	0.015 (2)	-0.0032 (18)
C8	0.053 (2)	0.049 (2)	0.057 (2)	0.0039 (16)	0.0256 (19)	-0.0011 (17)
C9	0.0499 (19)	0.054 (2)	0.057 (2)	0.0036 (16)	0.0259 (17)	-0.0019 (17)
C10	0.070 (3)	0.054 (2)	0.076 (3)	0.0024 (19)	0.022 (2)	0.003 (2)
C11	0.056 (2)	0.056 (2)	0.063 (2)	0.0018 (18)	0.023 (2)	0.0041 (19)
C12	0.084 (3)	0.079 (3)	0.073 (3)	-0.004 (2)	0.003 (2)	-0.001 (2)
C13	0.172 (5)	0.076 (4)	0.103 (4)	0.002 (3)	-0.012 (4)	-0.012 (3)
F1	0.0903 (17)	0.0681 (15)	0.149 (2)	-0.0148 (12)	0.0613 (17)	0.0074 (14)
F2	0.118 (2)	0.0605 (14)	0.109 (2)	0.0018 (12)	0.0492 (16)	-0.0211 (13)
F3	0.123 (2)	0.0591 (15)	0.108 (2)	0.0033 (13)	0.0028 (17)	0.0185 (13)
N1	0.0500 (18)	0.0519 (18)	0.0575 (18)	0.0012 (13)	0.0227 (16)	0.0024 (13)
O1	0.0707 (18)	0.0663 (18)	0.083 (2)	0.0126 (14)	0.0060 (15)	0.0000 (14)
O2	0.0701 (16)	0.0554 (16)	0.0701 (18)	-0.0010 (12)	0.0100 (14)	-0.0024 (13)

Geometric parameters (Å, °)

S1—C9	1.710 (3)	C8—C9	1.367 (4)
S1—C1	1.719 (3)	C8—C11	1.487 (5)
C1—N1	1.302 (4)	C9—C10	1.489 (5)
C1—C2	1.470 (5)	C10—F2	1.315 (4)
C2—C7	1.380 (4)	C10—F1	1.319 (4)
C2—C3	1.386 (5)	C10—F3	1.334 (4)
C3—C4	1.376 (5)	C11—O1	1.192 (4)
C3—H3	0.9300	C11—O2	1.321 (4)
C4—C5	1.369 (5)	C12—O2	1.459 (4)
C4—H4	0.9300	C12—C13	1.474 (5)
C5—C6	1.373 (5)	C12—H12A	0.9700
C5—H5	0.9300	C12—H12B	0.9700
C6—C7	1.373 (5)	C13—H13A	0.9600
C6—H6	0.9300	C13—H13B	0.9600
C7—H7	0.9300	C13—H13C	0.9600
C8—N1	1.367 (4)		
C9—S1—C1	89.59 (17)	C8—C9—S1	109.6 (3)
N1—C1—C2	123.2 (3)	C10—C9—S1	118.6 (3)
N1—C1—S1	114.6 (2)	F2—C10—F1	106.3 (3)
C2—C1—S1	122.2 (3)	F2—C10—F3	106.0 (3)
C7—C2—C3	119.1 (3)	F1—C10—F3	106.6 (3)
C7—C2—C1	119.7 (3)	F2—C10—C9	114.7 (3)
C3—C2—C1	121.1 (3)	F1—C10—C9	112.2 (3)
C4—C3—C2	120.3 (3)	F3—C10—C9	110.5 (3)
C4—C3—H3	119.8	O1—C11—O2	124.8 (4)
C2—C3—H3	119.8	O1—C11—C8	124.0 (3)
C5—C4—C3	120.0 (4)	O2—C11—C8	111.2 (3)
C5—C4—H4	120.0	O2—C12—C13	107.6 (4)
C3—C4—H4	120.0	O2—C12—H12A	110.2

C4—C5—C6	120.0 (4)	C13—C12—H12A	110.2
C4—C5—H5	120.0	O2—C12—H12B	110.2
C6—C5—H5	120.0	C13—C12—H12B	110.2
C5—C6—C7	120.4 (4)	H12A—C12—H12B	108.5
C5—C6—H6	119.8	C12—C13—H13A	109.5
C7—C6—H6	119.8	C12—C13—H13B	109.5
C6—C7—C2	120.1 (4)	H13A—C13—H13B	109.5
C6—C7—H7	119.9	C12—C13—H13C	109.5
C2—C7—H7	119.9	H13A—C13—H13C	109.5
N1—C8—C9	115.3 (3)	H13B—C13—H13C	109.5
N1—C8—C11	116.2 (3)	C1—N1—C8	110.9 (3)
C9—C8—C11	128.5 (3)	C11—O2—C12	115.9 (3)
C8—C9—C10	131.6 (3)		

Fig. 1

