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(5-Hydroxy-3-methyl-5-trifluoromethyl-4,5-dihydro-1*H*-pyrazol-1-yl)(2-hydroxyphenyl)-methanone

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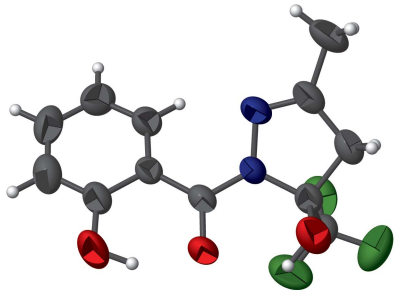
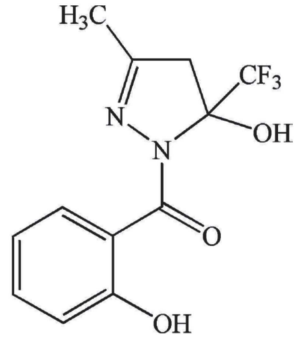
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{12}H_{11}F_3N_2O_3$, the hydroxyphenyl ring is twisted by 35.42 (11)° from the plane of the pyrazoline ring. The keto O atom is involved in two intramolecular O—H···O hydrogen bonds, which generate $S(6)$ loops. As result, a weak intramolecular C—H···N contact is formed, which generates an $S(7)$ ring motif. In the crystal, pairs of O—H···O hydrogen bonds link molecules into inversion dimers with an $R_2^2(16)$ motif. The dimers are linked by parallel-slipped π–π interactions [intercentroid distance = 3.8438 (19) Å], forming columns along the *c*-axis direction.

3D view



Chemical scheme



Structure description

Multifunctional ligands occupy a special place among the wide variety of organic ligands available (Filyakova *et al.*, 2010; Chizhov *et al.*, 2010; Chopin *et al.*, 2012). It has been shown that formation of cyclic products depends on the location of the trifluoromethyl group in the intermediate, for example a hydrazone, where intramolecular cyclization is realized *via* multiple bonds near the trifluoromethyl substituent (Pakal'nis *et al.*, 2008; 2014).

In the title compound, Fig. 1, the hydroxyphenyl ring (C5–C10) is twisted by 35.42 (11)° from the almost planar (r.m.s. deviation = 0.029 Å) pyrazoline ring (N1/N2/C1–C3). The keto-oxygen atom O2 acts as the acceptor for two intramolecular O1—H1···O2 and O3—H3···O2 hydrogen bonds (Table 1 and Fig. 1), which generate $S(6)$ graph-set motifs. As a result, a weak intramolecular C10—H10···N2 contact is formed between atom N2 and a phenyl C—H group, which generates an $S(7)$ graph-set motif

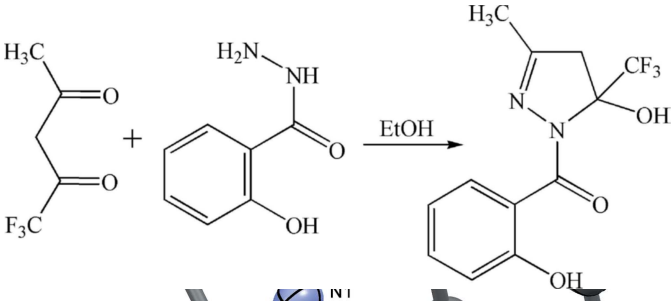


Figure 3
Reaction scheme.

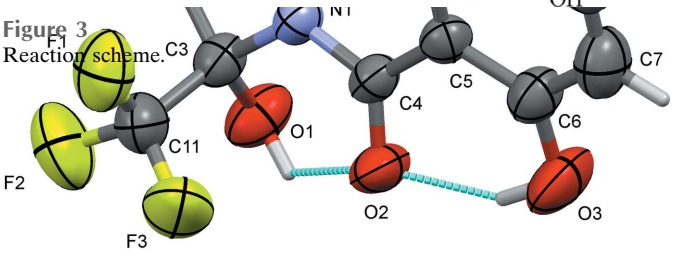


Figure 1
The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom labelling. Hydrogen bonds are shown as dashed lines (see Table 1 for details).

(Fig. 1 and Table 1). In the crystal, pairs of O1—H1···O3^{i} and O3—H3···O2^{i} hydrogen bonds [symmetry code: (i) $-x+1, -y+1, -z+1$] link molecules into inversion dimers, with an $R_2^2(16)$ ring motif for the former. The dimers stack along the *c*-axis direction, with parallel slipped π–π interactions [$Cg2\cdots Cg2^{i}$ = 3.8438 (19) Å; inter-planar distance = 3.4798 (13) Å; slippage 1.633 Å; *Cg*2 is the centroid of ring C5–C10], forming columns (Fig. 2).

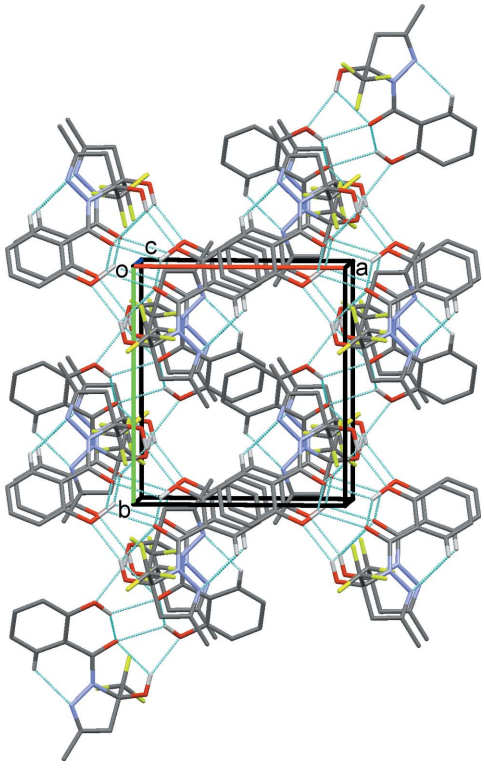


Figure 2
A view along the *c* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1 for details). For clarity, only the H atoms involved in hydrogen bonding have been included.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.90 (4)	2.18 (5)	2.753 (3)	120 (4)
O3—H3···O2	0.97 (5)	1.71 (5)	2.562 (3)	144 (4)
C10—H10···N2	0.93	2.35	2.892 (4)	117
O1—H1···O3^{i}	0.90 (4)	2.17 (5)	3.017 (3)	156 (5)
O3—H3···O2^{i}	0.97 (5)	2.31 (4)	2.887 (3)	118 (3)

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

Synthesis and crystallization

The synthesis of the title compound is illustrated in Fig. 3. In a 100 ml flask were mixed 1,1,1-trifluoropentandione-2,4 (5 mmol) with benzoylhydrazine (5 mmol) in ethanol. The flask was connected to a return refrigerator and heated for 1 h in a water bath. The reaction progress was monitored by thin layer chromatography (Silufol UV-254 plates). On completion of the reaction, after several days, two thirds of the solvent was

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{12}H_{11}F_3N_2O_3$
M_r	288.23
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, *b*, *c* (Å)	9.9339 (11), 10.6614 (9), 12.6802 (14)
β (°)	105.863 (11)
V (Å^3)	1291.8 (2)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.19
Crystal size (mm)	0.35 × 0.25 × 0.21
Data collection	
Diffractometer	Oxford Diffraction Xcalibur Ruby
Absorption correction	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.735, 0.779
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4867, 2618, 1558
R_{int}	0.035
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.631
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.050, 0.145, 1.04
No. of reflections	2618
No. of parameters	191
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.21

Computer programs: (*CrysAlis PRO*; Oxford Diffraction, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008), *OLEX2* (Dolomanov *et al.*, 2009).

removed at room temperature. The crystalline solid that formed were filtered off, washed with ethanol and dried in a vacuum desiccator over P_2O_5 (yield 85%). The compound was further recrystallized from ethanol solution to obtain colourless block-like crystals of the title compound suitable for X-ray diffraction analysis.

Refinement

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

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160316 [doi:10.1107/S2414314616003163]

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Crystal data

$C_{12}H_{11}F_3N_2O_3$
M_r = 288.23
Monoclinic, $P2_1/c$
a = 9.9339 (11) Å
b = 10.6614 (9) Å
c = 12.6802 (14) Å
β = 105.863 (11)°
V = 1291.8 (2) Å^3
Z = 4
$F(000)$ = 592
D_x = 1.482 Mg m^{-3}
Melting point: 401 K
Cu $K\alpha$ radiation, λ = 1.54184 Å
Cell parameters from 1180 reflections
θ = 4.1–72.2°
μ = 1.19 mm^{-1}
T = 293 K
Block, colourless
0.35 × 0.25 × 0.21 mm

Data collection

Oxford Diffraction Xcalibur Ruby diffractometer
Radiation source: Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 10.2576 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.735, T_{max} = 0.779
4867 measured reflections
2618 independent reflections
1558 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 76.6°, θ_{min} = 3.6°
h = −6→12
k = −13→13
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.145
S = 1.04
2618 reflections
191 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.1383P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0061 (6)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
H1	−0.058 (5)	0.266 (4)	0.410 (4)	0.143 (18)*
H3	0.128 (5)	0.527 (4)	0.565 (4)	0.146 (18)*
C5	0.3393 (3)	0.4086 (2)	0.5730 (2)	0.0481 (6)
C4	0.2129 (3)	0.3490 (2)	0.5019 (2)	0.0487 (6)
C3	0.0914 (3)	0.1690 (2)	0.3879 (2)	0.0535 (7)
C6	0.3238 (3)	0.5213 (3)	0.6259 (2)	0.0609 (7)
C10	0.4745 (3)	0.3655 (3)	0.5839 (2)	0.0599 (7)
H10	0.4873	0.2927	0.5474	0.072*
C2	0.1335 (3)	0.0304 (2)	0.3972 (3)	0.0627 (8)
H2A	0.0640	−0.0206	0.4181	0.075*
H2B	0.1460	−0.0008	0.3287	0.075*
C1	0.2680 (3)	0.0313 (3)	0.4847 (3)	0.0608 (7)
C9	0.5902 (3)	0.4277 (3)	0.6473 (3)	0.0763 (9)
H9	0.6797	0.3971	0.6536	0.092*
C8	0.5714 (4)	0.5362 (3)	0.7015 (3)	0.0786 (10)
H8	0.6485	0.5780	0.7457	0.094*
C7	0.4395 (4)	0.5822 (3)	0.6902 (3)	0.0776 (9)
H7	0.4279	0.6555	0.7265	0.093*
C11	0.0791 (3)	0.2168 (3)	0.2723 (3)	0.0706 (8)
C12	0.3472 (4)	−0.0863 (3)	0.5260 (3)	0.0865 (11)
H12A	0.3759	−0.1255	0.4675	0.130*
H12B	0.2881	−0.1427	0.5522	0.130*
H12C	0.4282	−0.0662	0.5848	0.130*
N1	0.2131 (2)	0.22809 (18)	0.46637 (18)	0.0497 (5)
N2	0.3114 (2)	0.1391 (2)	0.52323 (19)	0.0560 (6)
O2	0.10240 (19)	0.40885 (17)	0.46969 (17)	0.0657 (6)
O1	−0.0347 (2)	0.1838 (2)	0.4140 (2)	0.0718 (6)
O3	0.1975 (3)	0.5737 (2)	0.6185 (2)	0.0906 (8)
F1	0.1990 (2)	0.20268 (19)	0.24635 (16)	0.0927 (7)
F3	0.0475 (3)	0.3363 (2)	0.25789 (17)	0.1146 (9)
F2	−0.0157 (2)	0.1509 (2)	0.19893 (18)	0.1155 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C5	0.0536 (14)	0.0397 (13)	0.0509 (15)	0.0009 (11)	0.0139 (11)	0.0015 (11)
C4	0.0544 (15)	0.0393 (12)	0.0548 (15)	0.0056 (11)	0.0189 (12)	−0.0014 (11)
C3	0.0513 (14)	0.0486 (15)	0.0621 (17)	0.0001 (12)	0.0179 (12)	−0.0088 (12)
C6	0.0677 (18)	0.0484 (15)	0.0673 (19)	0.0012 (14)	0.0194 (14)	−0.0081 (14)

C10	0.0573 (16)	0.0495 (15)	0.0723 (19)	0.0000 (13)	0.0166 (14)	−0.0001 (14)
C2	0.0694 (19)	0.0455 (15)	0.078 (2)	−0.0038 (13)	0.0273 (16)	−0.0105 (14)
C1	0.0650 (17)	0.0432 (14)	0.081 (2)	0.0036 (13)	0.0322 (15)	−0.0041 (14)
C9	0.0606 (19)	0.071 (2)	0.093 (2)	−0.0063 (16)	0.0129 (17)	0.0089 (19)
C8	0.081 (2)	0.076 (2)	0.071 (2)	−0.0271 (19)	0.0084 (17)	−0.0070 (18)
C7	0.092 (2)	0.0642 (19)	0.076 (2)	−0.0145 (19)	0.0220 (18)	−0.0174 (17)
C11	0.074 (2)	0.069 (2)	0.0622 (19)	0.0048 (17)	0.0065 (16)	−0.0126 (16)
C12	0.085 (2)	0.0457 (16)	0.131 (3)	0.0165 (16)	0.033 (2)	0.0042 (19)
N1	0.0540 (12)	0.0382 (10)	0.0545 (13)	0.0043 (9)	0.0107 (10)	−0.0043 (9)
N2	0.0562 (13)	0.0427 (12)	0.0690 (15)	0.0088 (10)	0.0167 (11)	0.0015 (11)
O2	0.0573 (11)	0.0486 (11)	0.0844 (14)	0.0132 (9)	0.0078 (10)	−0.0103 (10)
O1	0.0564 (12)	0.0602 (13)	0.1058 (17)	−0.0032 (10)	0.0342 (11)	−0.0122 (12)
O3	0.0792 (16)	0.0614 (14)	0.130 (2)	0.0081 (12)	0.0259 (15)	−0.0378 (14)
F1	0.1130 (16)	0.0994 (15)	0.0793 (14)	−0.0102 (13)	0.0490 (12)	−0.0106 (11)
F3	0.175 (2)	0.0846 (15)	0.0776 (14)	0.0470 (15)	0.0225 (14)	0.0188 (11)
F2	0.1112 (17)	0.142 (2)	0.0742 (13)	−0.0210 (15)	−0.0062 (12)	−0.0247 (14)

Geometric parameters (Å, º)

C5—C4	1.475 (4)	C1—C12	1.497 (4)
C5—C6	1.405 (3)	C1—N2	1.277 (3)
C5—C10	1.390 (3)	C9—H9	0.9300
C4—N1	1.365 (3)	C9—C8	1.384 (4)
C4—O2	1.239 (3)	C8—H8	0.9300
C3—C2	1.532 (4)	C8—C7	1.370 (4)
C3—C11	1.525 (4)	C7—H7	0.9300
C3—N1	1.480 (3)	C11—F1	1.328 (4)
C3—O1	1.389 (3)	C11—F3	1.312 (4)
C6—C7	1.377 (4)	C11—F2	1.330 (3)
C6—O3	1.353 (3)	C12—H12A	0.9600
C10—H10	0.9300	C12—H12B	0.9600
C10—C9	1.379 (4)	C12—H12C	0.9600
C2—H2A	0.9700	N1—N2	1.411 (3)
C2—H2B	0.9700	O1—H1	0.90 (4)
C2—C1	1.486 (4)	O3—H3	0.97 (5)
C6—C5—C4	118.3 (2)	C10—C9—H9	120.4
C10—C5—C4	123.8 (2)	C10—C9—C8	119.2 (3)
C10—C5—C6	117.7 (3)	C8—C9—H9	120.4
N1—C4—C5	122.1 (2)	C9—C8—H8	119.9
O2—C4—C5	120.6 (2)	C7—C8—C9	120.2 (3)
O2—C4—N1	117.3 (2)	C7—C8—H8	119.9
C11—C3—C2	110.1 (2)	C6—C7—H7	119.6
N1—C3—C2	101.7 (2)	C8—C7—C6	120.9 (3)
N1—C3—C11	109.9 (2)	C8—C7—H7	119.6
O1—C3—C2	109.7 (2)	F1—C11—C3	111.0 (3)
O1—C3—C11	110.5 (2)	F1—C11—F2	106.2 (3)
O1—C3—N1	114.6 (2)	F3—C11—C3	114.3 (2)

C7—C6—C5	120.2 (3)	F3—C11—F1	105.8 (3)
O3—C6—C5	122.7 (3)	F3—C11—F2	108.6 (3)
O3—C6—C7	117.0 (3)	F2—C11—C3	110.6 (3)
C5—C10—H10	119.1	C1—C12—H12A	109.5
C9—C10—C5	121.8 (3)	C1—C12—H12B	109.5
C9—C10—H10	119.1	C1—C12—H12C	109.5
C3—C2—H2A	111.2	H12A—C12—H12B	109.5
C3—C2—H2B	111.2	H12A—C12—H12C	109.5
H2A—C2—H2B	109.1	H12B—C12—H12C	109.5
C1—C2—C3	102.8 (2)	C4—N1—C3	123.3 (2)
C1—C2—H2A	111.2	C4—N1—N2	122.0 (2)
C1—C2—H2B	111.2	N2—N1—C3	112.44 (19)
C2—C1—C12	122.3 (3)	C1—N2—N1	107.2 (2)
N2—C1—C2	115.6 (3)	C3—O1—H1	109 (3)
N2—C1—C12	122.0 (3)	C6—O3—H3	108 (3)
C5—C4—N1—C3	−174.9 (2)	C2—C3—N1—C4	−167.4 (2)
C5—C4—N1—N2	23.6 (3)	C2—C3—N1—N2	−4.4 (3)
C5—C6—C7—C8	1.7 (5)	C2—C1—N2—N1	−0.7 (3)
C5—C10—C9—C8	−0.2 (5)	C9—C8—C7—C6	0.5 (5)
C4—C5—C6—C7	−177.9 (3)	C11—C3—C2—C1	120.1 (3)
C4—C5—C6—O3	3.4 (4)	C11—C3—N1—C4	75.9 (3)
C4—C5—C10—C9	176.8 (3)	C11—C3—N1—N2	−121.1 (2)
C4—N1—N2—C1	166.7 (2)	C12—C1—N2—N1	179.9 (3)
C3—C2—C1—C12	177.4 (3)	N1—C3—C2—C1	3.6 (3)
C3—C2—C1—N2	−2.0 (3)	N1—C3—C11—F1	52.8 (3)
C3—N1—N2—C1	3.4 (3)	N1—C3—C11—F3	−66.8 (3)
C6—C5—C4—N1	−165.8 (2)	N1—C3—C11—F2	170.4 (2)
C6—C5—C4—O2	16.0 (4)	O2—C4—N1—C3	3.3 (4)
C6—C5—C10—C9	2.3 (4)	O2—C4—N1—N2	−158.2 (2)
C10—C5—C4—N1	19.8 (4)	O1—C3—C2—C1	−118.1 (3)
C10—C5—C4—O2	−158.4 (3)	O1—C3—C11—F1	−179.8 (2)
C10—C5—C6—C7	−3.1 (4)	O1—C3—C11—F3	60.7 (3)
C10—C5—C6—O3	178.1 (3)	O1—C3—C11—F2	−62.2 (3)
C10—C9—C8—C7	−1.3 (5)	O1—C3—N1—C4	−49.2 (3)
C2—C3—C11—F1	−58.4 (3)	O1—C3—N1—N2	113.8 (2)
C2—C3—C11—F3	−178.0 (3)	O3—C6—C7—C8	−179.4 (3)
C2—C3—C11—F2	59.1 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2	0.90 (4)	2.18 (5)	2.753 (3)	120 (4)
O3—H3···O2	0.97 (5)	1.71 (5)	2.562 (3)	144 (4)
C10—H10···N2	0.93	2.35	2.892 (4)	117

O1—H1···O3^{i}	0.90 (4)	2.17 (5)	3.017 (3)	156 (5)
O3—H3···O2^{i}	0.97 (5)	2.31 (4)	2.887 (3)	118 (3)

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