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## Structure Reports

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## 2-(Trifluoromethyl)benzoic acid

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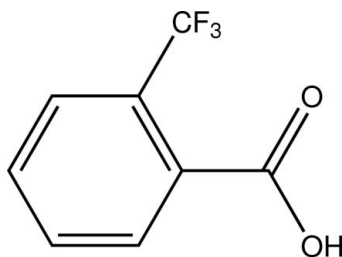
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 Key indicators: single-crystal X-ray study;  $T = 200$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.049;  $wR$  factor = 0.113; data-to-parameter ratio = 15.9.

In the title compound,  $\text{C}_8\text{H}_5\text{F}_3\text{O}_2$ , a halogenated derivative of benzoic acid, the carboxyl group is tilted by  $16.8(3)^\circ$  with respect to the plane of the aromatic ring. In the crystal,  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding gives rise to carboxylic acid dimers, which are further connected into double chains along  $[1,1/4,1]$  by  $\text{C}-\text{H}\cdots\text{O}$  contacts.  $\text{C}-\text{H}\cdots\text{F}$  and  $\text{C}-\text{F}\cdots\pi$  contacts are also observed.

## Related literature

For the crystal structure of benzoic acid using X-ray diffraction, see Bruno & Randaccio (1980). For the crystal structure of benzoic acid applying neutron radiation, see Wilson *et al.* (1996), and of *ortho*-fluorobenzoic acid, see Krausse & Dunken (1966). For the crystal structure of *ortho*-chlorobenzoic acid, see Ferguson & Sim (1961); Polito *et al.* (2008). For graph-set analysis of hydrogen bonds, see: Etter *et al.* (1990); Bernstein *et al.* (1995).



## Experimental

## Crystal data

 $\text{C}_8\text{H}_5\text{F}_3\text{O}_2$   
 $M_r = 190.12$   
 Monoclinic,  $P2_1/c$ 
 $a = 4.8816(3)$  Å  
 $b = 20.6948(14)$  Å  
 $c = 7.9697(5)$  Å

 $\beta = 109.544(4)^\circ$   
 $V = 758.74(8)$  Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation

 $\mu = 0.17$  mm<sup>-1</sup>  
 $T = 200$  K  
 $0.50 \times 0.50 \times 0.09$  mm

## Data collection

 Bruker APEXII CCD  
 diffractometer  
 7115 measured reflections

 1889 independent reflections  
 1548 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.113$   
 $S = 1.06$   
 1889 reflections

 119 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.30$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.33$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

 $C_g$  is the centroid of the C2–C7 ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{O2}^i$	0.84	1.81	2.6459 (19)	173
$\text{C6}-\text{H6}\cdots\text{O2}^{ii}$	0.95	2.66	3.590 (3)	167
$\text{C6}-\text{H6}\cdots\text{F3}^{iii}$	0.95	2.63	3.303 (3)	128
$\text{C7}-\text{H7}\cdots\text{O1}^{iii}$	0.95	2.66	3.411 (2)	137
$\text{C8}-\text{F1}\cdots\text{C}_g^{iv}$	1.34 (1)	3.48 (1)	4.806 (2)	170 (1)

 Symmetry codes: (i)  $-x + 3, -y, -z + 1$ ; (ii)  $x - 1, y, z - 1$ ; (iii)  $-x + 2, -y, -z$ ; (iv)  $x, -y - \frac{1}{2}, z - \frac{1}{2}$ .

Data collection: APEX2 (Bruker, 2010); cell refinement: SAINT (Bruker, 2010); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

The authors thank Mr Robert Bell for helpful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2339).

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## supporting information

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## 2-(Trifluoromethyl)benzoic acid

Richard Betz and Thomas Gerber

### S1. Comment

Benzoic acid has found widespread use as a ligand in coordination chemistry for a variety of transition metals and elements from the *s*- and *p*-block of the periodic system of the elements. It can act as a neutral or – upon deprotonation – an anionic ligand and serve as mono- or bidentate ligand. By varying the substituents on the phenyl moiety, the acidity of the carboxylic acid group can be fine-tuned. Particular interest rests in benzoic acid derivatives showing an asymmetric pattern of substituents on the aromatic moiety due to different possible orientations of the ligand in coordination compounds and the possible formation of stereoisomeric products. At the beginning of a comprehensive study aimed at rationalizing the coordination behaviour of various benzoic acid derivatives towards a number of transition metals in dependence of the *pH* value of the reaction batches it seemed interesting to determine the crystal structure of the title compound to enable comparative studies. The crystal structure of unsubstituted benzoic acid (Bruno & Randaccio (1980); Wilson *et al.* (1996)) as well as the crystal structures of benzoic acid derivatives bearing a halogen atom in an *ortho*-position to the carboxylic acid group (Krausse & Dunken (1966); Ferguson & Sim (1961); Polito *et al.* (2008)) are apparent in the literature.

C–C–C angles within the phenyl ring span a range of 118 ° to 121 ° with the biggest as well as the smallest angle found on both C-atoms in the *ortho*-position to the C-atom bearing the carboxylic acid group. The latter one is found on the carbon atom bearing the trifluoromethyl group (Fig. 1).

The carboxylic acid group is slightly tilted with respect to the plane of the aromatic moiety. The least-squares planes defined by their respective atoms enclose an angle of 16.81 (26) °.

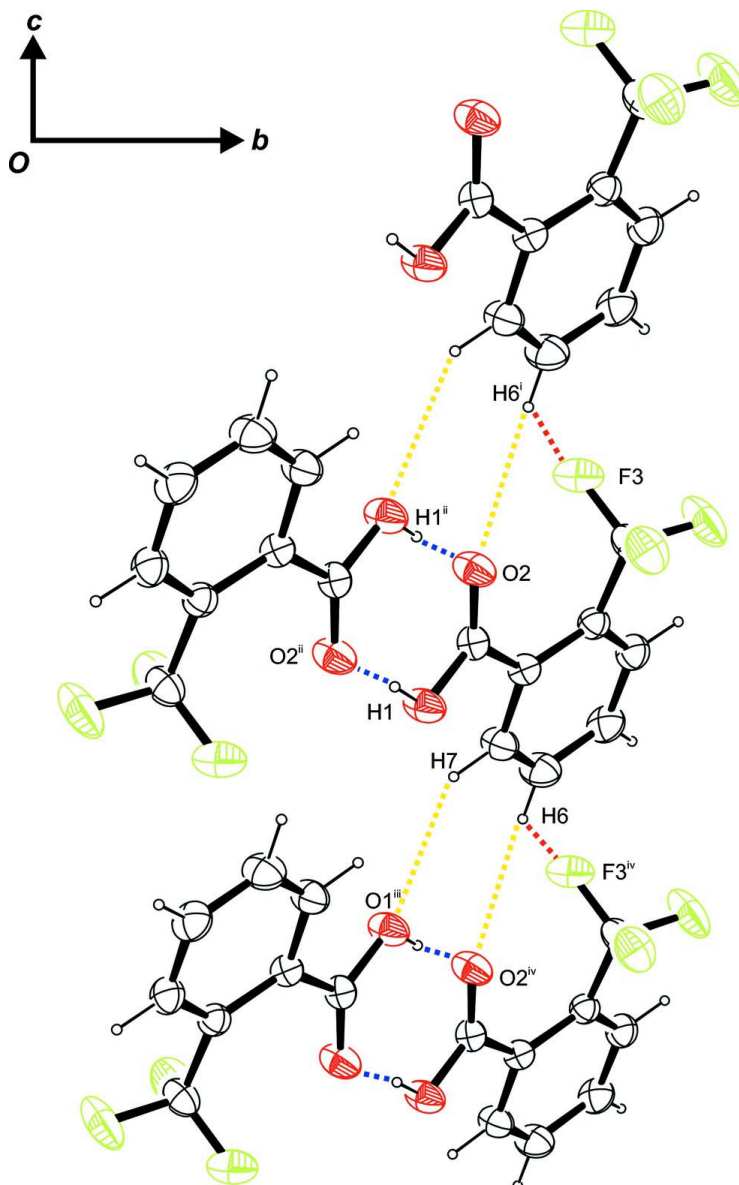
In the crystal structure, hydrogen bonds between the carboxylic acid groups of two molecules give rise to centrosymmetric dimers. These are further connected into double chains along [1 1/4 1] by C–H···O contacts whose range falls slightly below the sum of van-der-Waals radii of the corresponding atoms (Fig. 2). The latter contacts can be observed between the hydrogen atoms bonded to the carbon atoms in the *ortho*- as well as the *meta*-position to the carboxylic acid group and have the alcoholic as well as the carbonylic O-atom as acceptor. Additionally, the H-atom in the *meta*-position to the carboxylic acid group forms a contact to one of the fluorine atoms of the trifluoromethyl group. In terms of graph-set analysis (Etter *et al.* (1990); Bernstein *et al.* (1995).), the descriptor for the classical hydrogen bonds building the centrosymmetric dimers is  $R^2_2(8)$  on the unitary level while the C–H···O-contacts necessitate a  $C^1_1(6)R^2_2(10)$  descriptor on the same level. No  $\pi$ -stacking is obvious in the compound, however, a C–F···C<sub>g</sub> interaction (F···C<sub>g</sub>: 3.4803 (17) Å) can be observed.

The packing of the compound is shown in Figure 3.

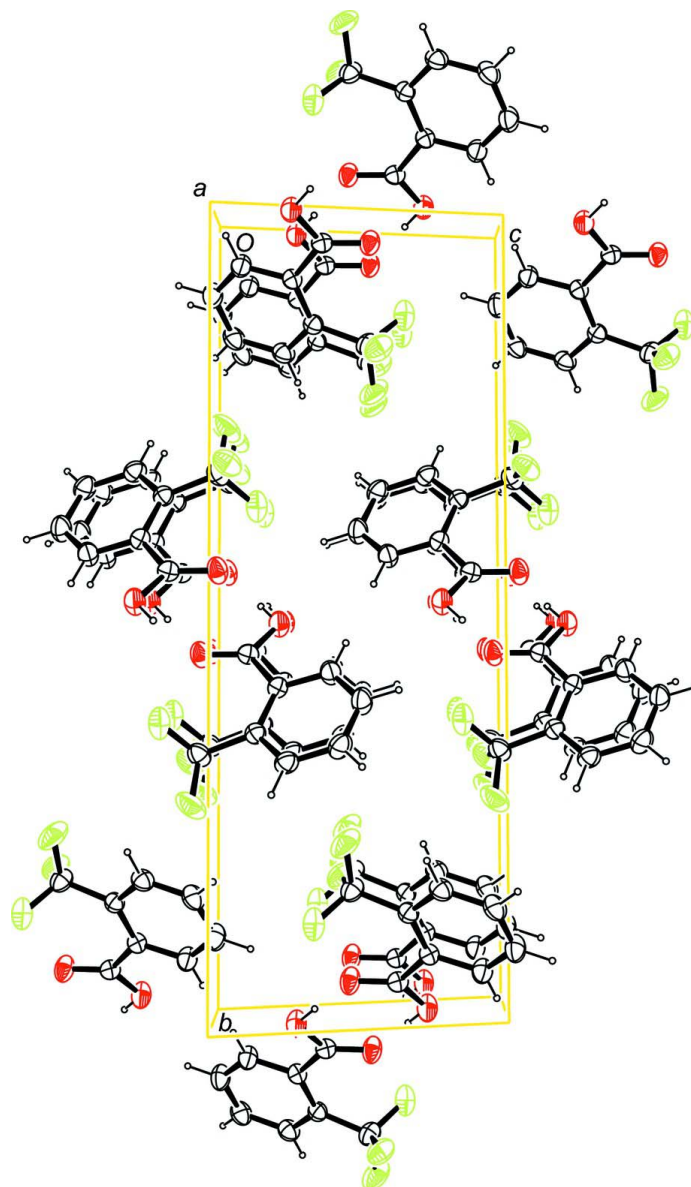
### S2. Experimental

The compound was obtained commercially (fluorochem). Crystals suitable for the X-ray diffraction study were grown from an aqueous solution of the compound.



**Figure 2**

Intermolecular contacts, viewed along  $[-1\ 0\ 0]$ . Hydrogen bonds are depicted with blue dashed lines, C-H...O contacts with yellow dashed lines and C-H...F contacts with red dashed lines. Symmetry operators: <sup>i</sup>  $x + 1, y, z + 1$ ; <sup>ii</sup>  $-x + 3, -y, -z + 1$ ; <sup>iii</sup>  $-x + 2, -y, -z$ ; <sup>iv</sup>  $x - 1, y, z - 1$ .

**Figure 3**

Molecular packing of the title compound, viewed along  $[-1\ 0\ 0]$  (anisotropic displacement ellipsoids drawn at 50% probability level).

**2-(Trifluoromethyl)benzoic acid***Crystal data* $C_8H_5F_3O_2$  $M_r = 190.12$ Monoclinic,  $P2_1/c$ Hall symbol:  $-P\ 2_1/c$  $a = 4.8816\ (3)\ \text{\AA}$  $b = 20.6948\ (14)\ \text{\AA}$  $c = 7.9697\ (5)\ \text{\AA}$  $\beta = 109.544\ (4)^\circ$  $V = 758.74\ (8)\ \text{\AA}^3$  $Z = 4$  $F(000) = 384$  $D_x = 1.664\ \text{Mg m}^{-3}$ Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$ 

Cell parameters from 4165 reflections

 $\theta = 2.7\text{--}28.3^\circ$  $\mu = 0.17\ \text{mm}^{-1}$

$T = 200$  K  
Platelet, colourless

$0.50 \times 0.50 \times 0.09$  mm

*Data collection*

Bruker APEXII CCD  
diffractometer  
Radiation source: fine-focus sealed tube  
Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
7115 measured reflections  
1889 independent reflections

1548 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$   
 $\theta_{\text{max}} = 28.3^\circ$ ,  $\theta_{\text{min}} = 3.4^\circ$   
 $h = -6 \rightarrow 6$   
 $k = -27 \rightarrow 27$   
 $l = -10 \rightarrow 10$

*Refinement*

Refinement on  $F^2$   
Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.113$   
 $S = 1.06$   
1889 reflections  
119 parameters  
0 restraints  
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  
 $w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 0.680P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{\AA}^{-3}$

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
F1	0.8290 (3)	0.22541 (7)	0.5490 (2)	0.0602 (5)
F2	1.2257 (3)	0.17857 (6)	0.56593 (18)	0.0453 (3)
F3	0.9086 (3)	0.12968 (7)	0.65393 (16)	0.0455 (3)
O1	1.2631 (3)	0.01372 (7)	0.27504 (18)	0.0366 (3)
H1	1.4044	-0.0080	0.3397	0.055*
O2	1.2658 (3)	0.05058 (7)	0.53681 (17)	0.0368 (3)
C1	1.1610 (4)	0.04997 (8)	0.3755 (2)	0.0262 (4)
C2	0.9025 (4)	0.08893 (8)	0.2720 (2)	0.0252 (3)
C3	0.7956 (4)	0.14205 (8)	0.3418 (2)	0.0264 (4)
C4	0.5485 (4)	0.17387 (9)	0.2361 (3)	0.0324 (4)
H4	0.4766	0.2097	0.2833	0.039*
C5	0.4046 (5)	0.15424 (10)	0.0626 (3)	0.0366 (4)
H5	0.2336	0.1761	-0.0078	0.044*
C6	0.5102 (5)	0.10294 (11)	-0.0075 (3)	0.0381 (5)
H6	0.4137	0.0897	-0.1268	0.046*
C7	0.7571 (4)	0.07086 (10)	0.0963 (2)	0.0329 (4)
H7	0.8292	0.0357	0.0467	0.040*
C8	0.9405 (4)	0.16805 (9)	0.5273 (3)	0.0334 (4)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
F1	0.0651 (10)	0.0483 (8)	0.0547 (8)	0.0222 (7)	0.0035 (7)	-0.0228 (7)
F2	0.0332 (7)	0.0462 (7)	0.0510 (7)	-0.0084 (5)	0.0069 (6)	-0.0134 (6)

F3	0.0422 (7)	0.0658 (9)	0.0285 (6)	0.0038 (6)	0.0119 (5)	-0.0006 (6)
O1	0.0363 (8)	0.0448 (8)	0.0270 (6)	0.0172 (6)	0.0084 (6)	-0.0008 (6)
O2	0.0342 (8)	0.0455 (8)	0.0255 (6)	0.0146 (6)	0.0034 (5)	-0.0036 (6)
C1	0.0231 (8)	0.0258 (8)	0.0293 (8)	0.0008 (6)	0.0083 (7)	-0.0006 (7)
C2	0.0227 (8)	0.0275 (8)	0.0254 (8)	0.0014 (6)	0.0081 (6)	0.0015 (7)
C3	0.0264 (9)	0.0269 (8)	0.0269 (8)	0.0000 (7)	0.0101 (7)	0.0009 (7)
C4	0.0331 (10)	0.0297 (9)	0.0352 (9)	0.0070 (7)	0.0126 (8)	0.0039 (8)
C5	0.0328 (10)	0.0389 (10)	0.0342 (10)	0.0091 (8)	0.0062 (8)	0.0081 (8)
C6	0.0358 (11)	0.0469 (11)	0.0266 (9)	0.0061 (9)	0.0036 (8)	-0.0002 (8)
C7	0.0331 (10)	0.0372 (10)	0.0270 (9)	0.0062 (8)	0.0080 (7)	-0.0023 (7)
C8	0.0300 (10)	0.0343 (10)	0.0341 (10)	0.0052 (8)	0.0084 (8)	-0.0065 (8)

*Geometric parameters (Å, °)*

F1—C8	1.341 (2)	C3—C4	1.385 (3)
F2—C8	1.339 (2)	C3—C8	1.509 (3)
F3—C8	1.333 (2)	C4—C5	1.386 (3)
O1—C1	1.311 (2)	C4—H4	0.9500
O1—H1	0.8400	C5—C6	1.378 (3)
O2—C1	1.214 (2)	C5—H5	0.9500
C1—C2	1.492 (2)	C6—C7	1.382 (3)
C2—C7	1.393 (2)	C6—H6	0.9500
C2—C3	1.409 (2)	C7—H7	0.9500
C1—O1—H1	109.5	C6—C5—H5	120.1
O2—C1—O1	122.74 (16)	C4—C5—H5	120.1
O2—C1—C2	123.96 (16)	C5—C6—C7	119.81 (19)
O1—C1—C2	113.29 (15)	C5—C6—H6	120.1
C7—C2—C3	118.36 (16)	C7—C6—H6	120.1
C7—C2—C1	117.59 (16)	C6—C7—C2	121.46 (18)
C3—C2—C1	124.05 (16)	C6—C7—H7	119.3
C4—C3—C2	119.55 (17)	C2—C7—H7	119.3
C4—C3—C8	117.00 (16)	F3—C8—F2	107.39 (16)
C2—C3—C8	123.43 (16)	F3—C8—F1	105.94 (17)
C3—C4—C5	121.01 (18)	F2—C8—F1	105.20 (16)
C3—C4—H4	119.5	F3—C8—C3	113.20 (16)
C5—C4—H4	119.5	F2—C8—C3	113.19 (16)
C6—C5—C4	119.79 (18)	F1—C8—C3	111.35 (16)
O2—C1—C2—C7	-162.52 (18)	C4—C5—C6—C7	0.8 (3)
O1—C1—C2—C7	16.4 (2)	C5—C6—C7—C2	0.4 (3)
O2—C1—C2—C3	16.7 (3)	C3—C2—C7—C6	-1.3 (3)
O1—C1—C2—C3	-164.37 (17)	C1—C2—C7—C6	177.90 (19)
C7—C2—C3—C4	1.1 (3)	C4—C3—C8—F3	108.95 (19)
C1—C2—C3—C4	-178.06 (17)	C2—C3—C8—F3	-72.5 (2)
C7—C2—C3—C8	-177.38 (18)	C4—C3—C8—F2	-128.55 (19)
C1—C2—C3—C8	3.4 (3)	C2—C3—C8—F2	50.0 (2)
C2—C3—C4—C5	0.0 (3)	C4—C3—C8—F1	-10.3 (3)

C8—C3—C4—C5	178.62 (18)	C2—C3—C8—F1	168.25 (18)
C3—C4—C5—C6	-1.0 (3)		

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

Cg is the centroid of the C2–C7 ring.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ O2 <sup>i</sup>	0.84	1.81	2.6459 (19)	173
C6—H6 $\cdots$ O2 <sup>ii</sup>	0.95	2.66	3.590 (3)	167
C6—H6 $\cdots$ F3 <sup>ii</sup>	0.95	2.63	3.303 (3)	128
C7—H7 $\cdots$ O1 <sup>iii</sup>	0.95	2.66	3.411 (2)	137
C8—F1 $\cdots$ Cg <sup>iv</sup>	1.34 (1)	3.48 (1)	4.806 (2)	170 (1)

Symmetry codes: (i)  $-x+3, -y, -z+1$ ; (ii)  $x-1, y, z-1$ ; (iii)  $-x+2, -y, -z$ ; (iv)  $x, -y-1/2, z-1/2$ .