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3,5-Difluorobenzoic acid

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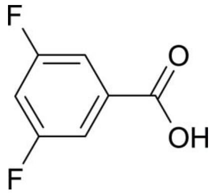
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.040; wR factor = 0.128; data-to-parameter ratio = 17.5.

The title compound, $C_7H_4O_2F_2$, forms dimers that are stabilized by hydrogen bonds between carboxyl groups. The crystal structure is stabilized by O—H···O and C—H···O hydrogen bonds, as well as weak stacking interactions between the molecules. The F atoms form edges of channels that extend along [100].

Related literature

For related literature, see: Dumas *et al.* (1999); Lynch & Salata (1998); Moffett & Tang (1968); Pinkus *et al.* (2003); Qadeer *et al.* (2007).



Experimental

Crystal data

$C_7H_4F_2O_2$
M_r = 158.10
Monoclinic, $P2_1/c$
a = 3.769 (1) Å
b = 13.400 (1) Å
c = 14.041 (1) Å
β = 93.78 (1)°
V = 707.6 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 293 (2) K
0.5 × 0.15 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (Otwinowski *et al.*, 2003)
T_{min} = 0.98, T_{max} = 0.99
18569 measured reflections
1817 independent reflections
1277 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.128
S = 1.07
1817 reflections
104 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.90 (2)	1.73 (2)	2.625 (1)	173 (2)
C4—H4···O2^{ii}	0.93	2.56	3.437 (2)	159

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

Data collection: *HKL-2000* (Otwinowski & Minor, 1997); cell refinement: *HKL-2000*; data reduction: *HKL-2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997) and *HKL-3000SM* (Minor *et al.*, 2006); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) and *HKL-3000SM*; molecular graphics: *HKL-3000SM*, *Mercury* (Macrae *et al.*, 2006), *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *HKL-3000SM*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2019).

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Dumas, J., Brittelli, D., Chen, J., Dixon, B., Hatoum-Mokdat, H., Konig, G., Sibley, R., Witowsky, J. & Wong, J. (1999). *J. Bioorg. Med. Chem. Lett.* **9**, 2531–2536.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Lynch, J. J. & Salata, J. J. (1998). US Patent No. 5 775 930; *Chem. Abstr.* **129**, 109, 102.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Minor, W., Cymborowski, M., Otwinowski, Z. & Chruszcz, M. (2006). *Acta Cryst.* D**62**, 859–866.
Moffett, R. B. & Tang, A. H. (1968). *J. Med. Chem.* **11**, 1020–1022.
Otwinowski, Z., Borek, D., Majewski, W. & Minor, W. (2003). *Acta Cryst.* A**59**, 228–234.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Pinkus, A. G., Kautz, J. A. & Ahobila-Vajjula, P. (2003). *J. Chem. Crystallogr.* **33**, 181–186.
Qadeer, G., Rama, N. H., Zareef, M. & Wong, W.-Y. (2007). *Acta Cryst.* E**63**, o1176–o1177.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

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supplementary materials

Acta Cryst. (2007). E**63**, o2754 [**doi:10.1107/S1600536807019861**]

3,5-Difluorobenzoic acid

W. Potrzebowski and **M. Chruszcz**

Comment

3,5-Difluorobenzoic acid (I) (Fig. 1) belongs to a family of compounds with medical and agricultural applications (Dumas *et al.*, 1999; Pinkus *et al.*, 2003). For example, substituted benzoic acids stimulate skeletal muscle (Moffett and Tang *et al.*, 1968) and thus 3,5-dichlorobenzoic acid has been used for derivative preparation in a cardiac arrhythmia treatment (Lynch and Salata, 1998). 3,5-Difluorobenzoic acid is used as a substrate in the synthesis of 3,5-difluorohydrazide (Qadeer *et al.*, 2007), which is needed for the synthesis of biologically active heterocyclic compounds.

3,5-Difluorobenzoic acid crystallized in the space group $P2_1/c$ with one molecule per asymmetric unit. The packing in the crystal structure of (I) is very similar to that observed for 3,5-dichlorobenzoic acid (Pinkus *et al.*, 2003). In both cases the carboxylic acid groups are involved in dimer formation, by forming stabilizing hydrogen bonds (Table 1, Fig. 2). The packing is also stabilized by intermolecular C4—H4···O2 hydrogen-bond interactions (Table 1). Stacking interactions are weak with distances between centroids and offsets of 3.77Å and 1.37Å respectively. The molecules of (I) are packed in such a way that channels of 2.6Å by 3.3Å wide are formed between halogen substituents (Fig. 2). The volume of the channels in each unit cell, as calculated with PLATON (Spek, 2003), equals 8% of the unit cell volume. The carboxylic acid and benzene groups are almost coplanar with a C2—C1—C7—O2 torsion angle equal to 172°.

Experimental

3,5-Difluorobenzoic acid (97%) was purchased from Aldrich. It was initially dissolved in acetone, and small crystals were obtained by slow evaporation at 293 K. These crystals of I were dissolved in and then recrystallized by evaporation from 1-butanol, which resulted in single crystals suitable for X-ray diffraction study.

Refinement

The aromatic hydrogen atoms were visible in the difference density Fourier map, but during refinement they were replaced in ideal positions with C—H distances equal to 0.93Å and were allowed to refine using the riding model with an isotropic displacement parameter 1.2 times that of the adjacent carbon atom. The hydrogen atom of the carboxylic acid group was localized from the difference map and isotropically refined. The O—H distance was restrained to be 0.82 Å.

Figures

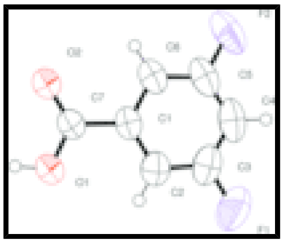

Fig. 1. A view of the title compound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of an arbitrary radius.

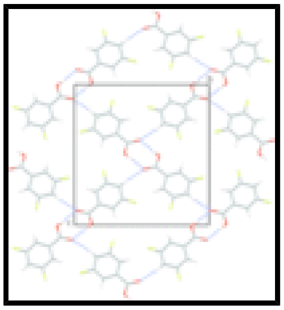

Fig. 2. The molecular packing of compound I shown along [100]. Hydrogen bonds are marked with blue, dashed lines.

3,5-difluorobenzoic acid

Crystal data

$C_7H_4F_2O_2$

$M_r = 158.10$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 3.769$ (1) Å

$b = 13.400$ (1) Å

$c = 14.041$ (1) Å

$\beta = 93.78$ (1)°

$V = 707.6$ (2) Å^3

$Z = 4$

$F_{000} = 320$

$D_x = 1.484$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71074$ Å

Cell parameters from 18569 reflections

$\theta = 2.1$–28.7°

$\mu = 0.14$ mm^{-1}

$T = 293$ (2) K

Needle, colorless

0.5 × 0.15 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 10 pixels mm^{-1}

$T = 293(2)$ K

ω scans with χ offset

Absorption correction: multi-scan (Otwinowski *et al.*, 2003)

$T_{\min} = 0.98$, $T_{\max} = 0.99$

18569 measured reflections

1817 independent reflections

1277 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.033$

$\theta_{\max} = 28.7$°

$\theta_{\min} = 2.1$°

$h = -5 \rightarrow 5$

$k = -17 \rightarrow 17$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.0698P]$
where $P = (F_o^2 + 2F_c^2)/3$

$wR(F^2)$ = 0.128

S = 1.07

1817 reflections

104 parameters

1 restraint

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

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

$\Delta\rho_{\max}$ = 0.16 e Å^{-3}

$\Delta\rho_{\min}$ = −0.16 e Å^{-3}

Extinction correction: none

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.

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 > 2sigma(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 (Å^2)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
O2	0.1841 (3)	0.48378 (7)	0.39611 (7)	0.0784 (3)
O1	−0.0234 (3)	0.36856 (8)	0.49171 (7)	0.0747 (3)
C7	0.1216 (3)	0.39595 (10)	0.41548 (8)	0.0586 (3)
C1	0.2106 (3)	0.31418 (10)	0.34960 (9)	0.0597 (3)
C6	0.3240 (3)	0.33876 (12)	0.26072 (9)	0.0691 (4)
H6	0.3440	0.4050	0.2421	0.083*
F2	0.5187 (3)	0.28467 (10)	0.11447 (7)	0.1159 (4)
C4	0.3797 (4)	0.16402 (14)	0.22527 (13)	0.0893 (5)
H4	0.4364	0.1135	0.1835	0.107*
C2	0.1801 (4)	0.21588 (11)	0.37749 (11)	0.0724 (4)
H2	0.1043	0.1993	0.4372	0.087*
F1	0.2359 (4)	0.04641 (8)	0.33917 (11)	0.1330 (5)
C5	0.4060 (4)	0.26214 (14)	0.20097 (10)	0.0800 (5)
C3	0.2666 (5)	0.14321 (12)	0.31326 (14)	0.0867 (5)
H1	−0.071 (6)	0.4223 (13)	0.5270 (15)	0.135 (8)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.1051 (8)	0.0638 (6)	0.0701 (6)	−0.0015 (5)	0.0341 (5)	−0.0054 (4)
O1	0.0966 (7)	0.0682 (6)	0.0624 (6)	0.0010 (5)	0.0283 (5)	−0.0038 (4)
C7	0.0591 (7)	0.0647 (8)	0.0529 (6)	0.0031 (5)	0.0103 (5)	−0.0040 (5)
C1	0.0526 (6)	0.0686 (8)	0.0581 (7)	0.0034 (5)	0.0047 (5)	−0.0124 (5)
C6	0.0631 (7)	0.0854 (9)	0.0596 (7)	0.0001 (6)	0.0096 (6)	−0.0150 (6)

F2	0.1198 (9)	0.1598 (11)	0.0716 (6)	−0.0067 (7)	0.0334 (5)	−0.0382 (6)
C4	0.0775 (10)	0.1029 (13)	0.0870 (11)	0.0128 (8)	0.0021 (8)	−0.0437 (9)
C2	0.0750 (8)	0.0692 (9)	0.0727 (8)	0.0050 (7)	0.0030 (6)	−0.0109 (6)
F1	0.1841 (13)	0.0705 (7)	0.1448 (11)	0.0127 (7)	0.0135 (9)	−0.0238 (6)
C5	0.0657 (8)	0.1118 (13)	0.0634 (8)	0.0016 (8)	0.0100 (6)	−0.0282 (8)
C3	0.0903 (11)	0.0692 (9)	0.0996 (12)	0.0093 (8)	−0.0024 (9)	−0.0239 (8)

Geometric parameters (Å, °)

O2—C7	1.2341 (15)	F2—C5	1.3471 (19)
O1—C7	1.2870 (15)	C4—C3	1.362 (3)
O1—H1	0.898 (15)	C4—C5	1.364 (3)
C7—C1	1.4865 (17)	C4—H4	0.9300
C1—C2	1.381 (2)	C2—C3	1.381 (2)
C1—C6	1.3853 (19)	C2—H2	0.9300
C6—C5	1.374 (2)	F1—C3	1.354 (2)
C6—H6	0.9300		
C7—O1—H1	109.9 (15)	C3—C4—H4	121.4
O2—C7—O1	123.58 (11)	C5—C4—H4	121.4
O2—C7—C1	120.76 (11)	C3—C2—C1	117.37 (16)
O1—C7—C1	115.66 (12)	C3—C2—H2	121.3
C2—C1—C6	121.24 (13)	C1—C2—H2	121.3
C2—C1—C7	120.01 (12)	F2—C5—C4	118.30 (14)
C6—C1—C7	118.75 (13)	F2—C5—C6	118.69 (17)
C5—C6—C1	117.88 (15)	C4—C5—C6	123.01 (16)
C5—C6—H6	121.1	F1—C3—C4	118.50 (15)
C1—C6—H6	121.1	F1—C3—C2	118.17 (18)
C3—C4—C5	117.18 (14)	C4—C3—C2	123.33 (17)
O2—C7—C1—C2	171.99 (12)	C3—C4—C5—F2	179.73 (13)
O1—C7—C1—C2	−8.38 (18)	C3—C4—C5—C6	−0.1 (2)
O2—C7—C1—C6	−7.93 (19)	C1—C6—C5—F2	−179.63 (12)
O1—C7—C1—C6	171.70 (12)	C1—C6—C5—C4	0.2 (2)
C2—C1—C6—C5	−0.1 (2)	C5—C4—C3—F1	179.64 (15)
C7—C1—C6—C5	179.81 (12)	C5—C4—C3—C2	−0.1 (3)
C6—C1—C2—C3	−0.1 (2)	C1—C2—C3—F1	−179.56 (14)
C7—C1—C2—C3	−179.99 (13)	C1—C2—C3—C4	0.2 (2)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^{i}	0.90 (2)	1.73 (2)	2.625 (1)	173 (2)
C4—H4···O2^{ii}	0.93	2.56	3.437 (2)	159

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) −*x*+1, *y*−1/2, −*z*+1/2.

Fig. 1

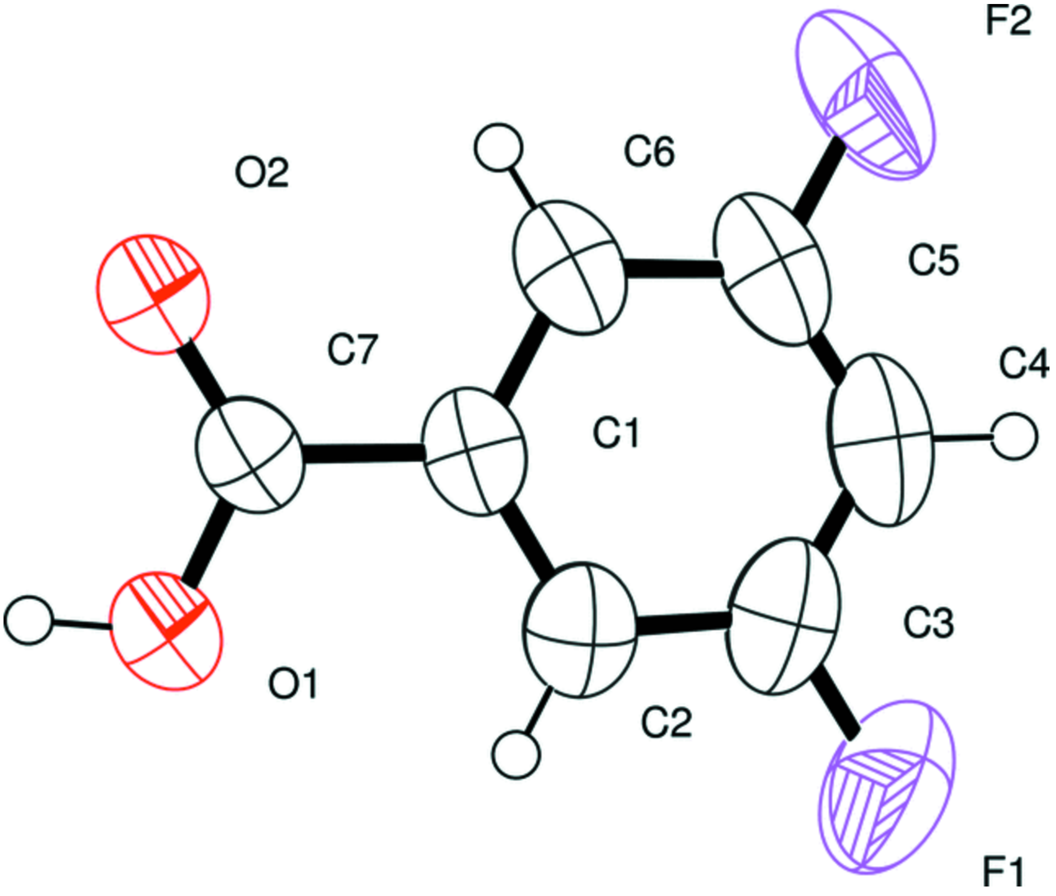

Fig. 2