organic compounds

2,3-Difluorobenzoic acid

Aleksandra A. Knapik, Wladek Minor and Maksymilian Chruszcz*

University of Virginia, Department of Molecular Physiology and Biological Physics, 1340 Jefferson Park Avenue, Charlottesville, VA 22908, USA

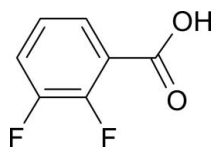Correspondence e-mail: maks@iwonka.med.virginia.edu

2,3-Difluorobenzoic acid, $C_7H_4F_2O_2$, forms dimers that are stabilized by hydrogen bonds. The dimers are stacked and the stacks are held together by weak C—H⋯F and C—H⋯O interactions.

Related literature

For related literature, see: Juhler & Mortensen (2002); Malone *et al.* (2006); Potrzebowski & Chruszcz (2007).

Experimental

Crystal data

$C_7H_4F_2O_2$
M_r = 158.10
Monoclinic, $P2_1/c$
a = 3.761 (1) Å
b = 6.520 (1) Å
c = 26.521 (2) Å
β = 92.27 (1)°

V = 649.8 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 293 (2) K
$0.15 \times 0.15 \times 0.02$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer

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

T_{min} = 0.98, T_{max} = 1.00 (expected range = 0.977–0.997)
25713 measured reflections

1881 independent reflections
1371 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.133
S = 1.06
1881 reflections

116 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C5—H5⋯O1^i	0.94 (2)	2.65 (2)	3.509 (2)	153 (2)
O2—H2⋯O1^{ii}	1.03 (3)	1.60 (3)	2.625 (2)	173 (3)
C6—H6⋯O2^{iii}	0.95 (2)	2.67 (2)	3.498 (2)	146 (1)
C4—H4⋯F2^{iv}	0.95 (2)	2.65 (2)	3.513 (2)	151 (2)

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

Data collection: *HKL-2000* (Otwinowski & Minor, 1997); cell refinement: *HKL-2000*; data reduction: *HKL-2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *HKL-3000SM* (Minor *et al.*, 2006); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) 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*.

References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Juhler, R. K. & Mortensen, A. P. (2002). *J. Chromatogr. A*, **957**, 11–16.
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.
Malone, S., Broacha, E., Shaw, D. & Hampton, T. (2006). US Patent 7 032 662.
Minor, W., Cymborowski, M., Otwinowski, Z. & Chruszcz, M. (2006). *Acta Cryst.* D**62**, 859–866.
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.
Potrzebowski, W. & Chruszcz, M. (2007). *Acta Cryst.* E**63**, o2754.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supplementary materials

2,3-Difluorobenzoic acid

A. A. Knapik, W. Minor and M. Chruszcz

Comment

2,3-Difluorobenzoic acid (I) (Fig. 1) is used as a tracer for determining the extent of recovery of materials injected into oil wells (Malone *et al.*, 2006) or for observing water movment in soil (Juhler & Mortensen, 2002). 2,3-Difluorobenzoic acid crystallized, like 3,5-difluorobenzoic acid (Potrzebowski & Chruszcz, 2007), in the space group $P2_1/c$ with one molecule per asymmetric unit. Both (I) and 3,5-difluorobenzoic acid form dimers in the crystal lattice (Fig. 2), but the dimers of the two compounds pack differently. The molecules of (I) pack more tightly in the crystal, as the crystal density is 8% higher than in case of 3,5-difluorobenzoic acid. The dimers of (I) are stabilized by hydrogen bonds (Table 1). The dimers are arranged in stacks that are held together by weak C—H⋯F and C—H⋯O interactions (Fig. 2).

Experimental

2,3-Difluorobenzoic acid (98%) was purchased from Aldrich, and dissolved in 1-propanol. Single crystals suitable for X-ray diffraction study were obtained by slow evaporation at 293 K.

Refinement

All hydrogen atoms were localized using the difference density Fourier map. Their positions and isotropic displacement parameters were refined.
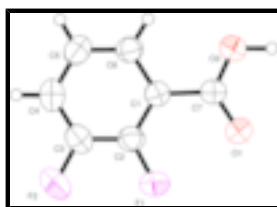
Figures

Fig. 1. An asymmetric unit of 2,3-difluorobenzoic acid. Displacement ellipsoids are drawn at the 50% probability level, while hydrogen atoms are drawn as spheres of an arbitrary radius.
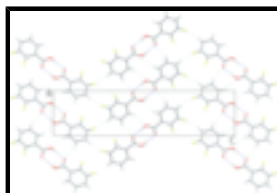

Fig. 2. The packing of 2,3-difluorobenzoic acid shown along [010]. Hydrogen bonds are marked with blue, dashed lines. Weak C—H⋯F and C—H⋯O interactions are shown as light-blue, dashed lines.

2,3-difluorobenzoic acid

Crystal data

$C_7H_4F_2O_2$	$F_{000} = 320$
$M_r = 158.10$	$D_x = 1.616$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71074$ Å
Hall symbol: -P 2ybc	Cell parameters from 25713 reflections
$a = 3.761$ (1) Å	$\theta = 3.1–30.0º$
$b = 6.520$ (1) Å	$\mu = 0.15$ mm^{-1}
$c = 26.521$ (2) Å	$T = 293$ (2) K
$\beta = 92.27$ (1)º	Plate, colorless
$V = 649.8$ (2) Å^3	$0.15 \times 0.15 \times 0.02$ mm
$Z = 4$	

Data collection

Rigaku R-AXIS RAPID diffractometer	1881 independent reflections
Radiation source: fine-focus sealed tube	1371 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.031$
Detector resolution: 10 pixels mm^{-1}	$\theta_{max} = 30.0º$
$T = 293(2)$ K	$\theta_{min} = 3.1º$
ω scans with χ offset	$h = -5\rightarrow5$
Absorption correction: multi-scan (Otwinowski *et al.*, 2003)	$k = -9\rightarrow9$
$T_{min} = 0.98$, $T_{max} = 1.00$	$l = -37\rightarrow37$
25713 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.044$	All H-atom parameters refined
$wR(F^2) = 0.133$	$w = 1/[\sigma^2(F_o^2) + (0.0665P)^2 + 0.0891P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
1881 reflections	$\Delta\rho_{max} = 0.29$ e Å^{-3}
116 parameters	$\Delta\rho_{min} = -0.13$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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.

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.3028 (3)	0.18896 (18)	0.09787 (4)	0.0453 (3)
C2	0.3710 (3)	0.2435 (2)	0.14793 (5)	0.0507 (3)
C3	0.2895 (4)	0.1088 (2)	0.18600 (5)	0.0580 (3)
C4	0.1428 (4)	−0.0797 (2)	0.17592 (6)	0.0607 (4)
C5	0.0737 (4)	−0.1357 (2)	0.12626 (6)	0.0587 (3)
C6	0.1521 (3)	−0.0033 (2)	0.08785 (5)	0.0517 (3)
C7	0.3892 (3)	0.32666 (19)	0.05550 (5)	0.0485 (3)
F1	0.5159 (3)	0.42443 (14)	0.16134 (3)	0.0748 (3)
F2	0.3611 (3)	0.16829 (19)	0.23412 (3)	0.0893 (4)
O1	0.5592 (3)	0.48801 (16)	0.06313 (4)	0.0673 (3)
O2	0.2818 (3)	0.26822 (19)	0.01143 (4)	0.0742 (4)
H2	0.330 (8)	0.372 (4)	−0.0169 (13)	0.158 (11)*
H4	0.090 (5)	−0.174 (3)	0.2020 (8)	0.087 (6)*
H5	−0.026 (5)	−0.264 (3)	0.1183 (7)	0.079 (5)*
H6	0.104 (4)	−0.037 (3)	0.0534 (6)	0.057 (4)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0441 (6)	0.0446 (6)	0.0472 (6)	0.0012 (5)	0.0014 (4)	−0.0005 (5)
C2	0.0550 (7)	0.0465 (6)	0.0503 (6)	0.0009 (5)	0.0003 (5)	−0.0037 (5)
C3	0.0635 (8)	0.0653 (8)	0.0451 (6)	0.0066 (6)	0.0024 (5)	0.0018 (6)
C4	0.0593 (7)	0.0625 (8)	0.0607 (8)	0.0018 (6)	0.0074 (6)	0.0151 (6)
C5	0.0565 (7)	0.0494 (7)	0.0699 (9)	−0.0047 (6)	0.0003 (6)	0.0058 (6)
C6	0.0524 (7)	0.0495 (7)	0.0529 (7)	−0.0036 (5)	−0.0017 (5)	−0.0021 (5)
C7	0.0503 (6)	0.0481 (6)	0.0471 (6)	−0.0027 (5)	0.0001 (5)	−0.0024 (5)
F1	0.1091 (7)	0.0572 (5)	0.0576 (5)	−0.0162 (5)	−0.0039 (5)	−0.0095 (4)
F2	0.1270 (9)	0.0956 (8)	0.0449 (5)	−0.0067 (7)	0.0015 (5)	−0.0011 (5)
O1	0.0901 (7)	0.0569 (6)	0.0544 (5)	−0.0240 (5)	−0.0021 (5)	0.0016 (4)
O2	0.1028 (9)	0.0728 (7)	0.0461 (5)	−0.0317 (6)	−0.0058 (5)	0.0013 (5)

Geometric parameters (Å, °)

C1—C2	1.3885 (17)	C4—H4	0.95 (2)
C1—C6	1.3968 (17)	C5—C6	1.376 (2)
C1—C7	1.4842 (17)	C5—H5	0.94 (2)
C2—F1	1.3415 (16)	C6—H6	0.950 (16)
C2—C3	1.3819 (19)	C7—O1	1.2435 (16)
C3—F2	1.3508 (16)	C7—O2	1.2796 (15)
C3—C4	1.369 (2)	O2—H2	1.03 (3)
C4—C5	1.381 (2)		
C2—C1—C6	118.03 (12)	C5—C4—H4	119.0 (12)
C2—C1—C7	122.09 (11)	C6—C5—C4	120.17 (14)
C6—C1—C7	119.88 (11)	C6—C5—H5	119.2 (12)
F1—C2—C3	117.71 (12)	C4—C5—H5	120.6 (11)
F1—C2—C1	122.43 (12)	C5—C6—C1	121.28 (13)
C3—C2—C1	119.86 (12)	C5—C6—H6	122.0 (10)
F2—C3—C4	120.41 (13)	C1—C6—H6	116.8 (10)
F2—C3—C2	117.76 (14)	O1—C7—O2	122.84 (12)
C4—C3—C2	121.82 (13)	O1—C7—C1	121.00 (11)
C3—C4—C5	118.84 (13)	O2—C7—C1	116.15 (11)
C3—C4—H4	122.2 (12)	C7—O2—H2	114.3 (16)
C6—C1—C2—F1	179.84 (11)	C2—C3—C4—C5	−0.2 (2)
C7—C1—C2—F1	0.6 (2)	C3—C4—C5—C6	0.0 (2)
C6—C1—C2—C3	−0.03 (19)	C4—C5—C6—C1	0.2 (2)
C7—C1—C2—C3	−179.23 (12)	C2—C1—C6—C5	−0.17 (19)
F1—C2—C3—F2	0.0 (2)	C7—C1—C6—C5	179.05 (12)
C1—C2—C3—F2	179.88 (12)	C2—C1—C7—O1	7.3 (2)
F1—C2—C3—C4	−179.64 (13)	C6—C1—C7—O1	−171.85 (12)
C1—C2—C3—C4	0.2 (2)	C2—C1—C7—O2	−173.28 (12)
F2—C3—C4—C5	−179.87 (13)	C6—C1—C7—O2	7.53 (18)

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···O1[i]	0.94 (2)	2.65 (2)	3.509 (2)	153 (2)
O2—H2···O1[ii]	1.03 (3)	1.60 (3)	2.625 (2)	173 (3)
C6—H6···O2[iii]	0.95 (2)	2.67 (2)	3.498 (2)	146 (1)
C4—H4···F2[iv]	0.95 (2)	2.65 (2)	3.513 (2)	151 (2)

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

Fig. 1

Fig. 2