Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(2*S*,4*R*)-4-Fluoropyrrolidinium-2-carboxylate

David B. Hobart Jr* and Joseph S. Merola

Department of Chemistry, Virginia Tech, Blacksburg, VA 24061, USA
Correspondence e-mail: dhobart@vt.edu

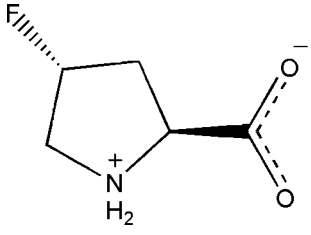
Received 27 June 2012; accepted 11 July 2012

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.073; data-to-parameter ratio = 8.4.

The crystal structure of the title compound, $C_5H_8FNO_2$, at 100 K, displays intermolecular N—H···O hydrogen bonding between the ammonium and carboxylate groups as a result of its zwitterionic nature in the solid state. The five-membered ring adopts an envelope conformation with the C atom at the 3-position as the flap. The compound is of interest with respect to the synthesis and structural properties of synthetic collagens. The absolute structure was determined by comparison with the commercially available material.

Related literature

For the synthesis of the title compound, see: Gottlieb *et al.* (1965); Azad *et al.* (2012). For its applications and properties with respect to synthetic collagens, see: Hodges & Raines (2003, 2005); Holmgren *et al.* (1999); Kim *et al.* (2005); Mooney *et al.* (2002); Persikov *et al.* (2003); Raines (2005); Shoulders & Raines (2009); Shoulders *et al.* (2006); Takeuchi & Prockop (1969).



Experimental

Crystal data

$C_5H_8FNO_2$
M_r = 133.12
Orthorhombic, $P2_12_12_1$
a = 7.6530 (6) Å
b = 8.4128 (6) Å
c = 8.6286 (6) Å
V = 555.54 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.14 mm^{-1}
T = 100 K
0.26 × 0.05 × 0.03 mm

Data collection

Oxford Diffraction Gemini Ultra diffractometer
Absorption correction: Gaussian (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.977, T_{max} = 0.996
10227 measured reflections
959 independent reflections
832 reflections with $I > 2\sigma(I)$
R_{int} = 0.082

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.073
S = 1.07
959 reflections
114 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H6B···O2^{i}	0.92 (3)	1.90 (3)	2.744 (2)	152 (2)
N6—H6A···O2^{ii}	0.91 (3)	2.01 (3)	2.899 (2)	164 (2)

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

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

The authors would like to thank the Virginia Tech Department of Chemistry and the Virginia Tech Crystallography Laboratory for their support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2392).

References

Agilent (2011). *CrysAlis PRO*. Agilent Technologies UK Ltd, Yarnton, Oxfordshire, England.
Azad, B. B., Ashique, R., Labiris, N. R. & Chirakal, R. (2012). *J. Labelled Compd. Radiopharm.* **55**, 23–28.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Gottlieb, A. A., Fujita, Y., Udenfriend, S. & Witkop, B. (1965). *Biochemistry*, **4**, 2507–2513.
Hodges, J. A. & Raines, R. T. (2003). *J. Am. Chem. Soc.* **125**, 9262–9263.
Hodges, J. A. & Raines, R. T. (2005). *J. Am. Chem. Soc.* **127**, 15923–15932.
Holmgren, S. K., Bretscher, L. E., Taylor, K. M. & Raines, R. T. (1999). *Chem. Biol.* **6**, 63–70.
Kim, W., McMillan, R. A., Snyder, J. P. & Conticello, V. P. (2005). *J. Am. Chem. Soc.* **127**, 18121–18132.
Mooney, S. D., Kollman, P. A. & Klein, T. E. (2002). *Biopolymers*, **64**, 63–71.
Persikov, A. V., Ramshaw, J. A. M., Kirkpatrick, A. & Brodsky, B. (2003). *J. Am. Chem. Soc.* **125**, 11500–11501.
Raines, R. T. (2005). *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)*, **46**, 181–182.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shoulders, M. D., Hodges, J. A. & Raines, R. T. (2006). *J. Am. Chem. Soc.* **128**, 8112–8113.
Shoulders, M. D. & Raines, R. T. (2009). *Adv. Exp. Med. Biol.* **611**, 251–252.
Takeuchi, T. & Prockop, D. J. (1969). *Biochim. Biophys. Acta Protein Struct.* **175**, 142–155.

supplementary materials

Acta Cryst. (2012). E**68**, o2490 [doi:10.1107/S1600536812031741]

(2*S*,4*R*)-4-Fluoropyrrolidinium-2-carboxylate

David B. Hobart Jr and Joseph S. Merola

Comment

The title compound is a useful building block in the synthesis of synthetic collagens. Collagen is the most abundant protein found in animals and exists as a triple helix comprised of three strands. The amino acid encoding of the strands follows the *X*—Y-Gly pattern. Trans-4-fluoroproline has been shown to induce hyperstability of the triple helix when substituted for the Y codon.

Experimental

The title compound was purchased commercially from Bachem Americas, Inc., 3132 Kashiwa Street, Torrance, CA 90505 USA. Single crystals suitable for diffraction were grown *via* slow evaporation from a 50/50 (*v*/*v*) solution of acetone and water.

Refinement

No Flack parameter is reported as Friedel pairs were merged *via* MERG3 instruction due to the absence of anomalous dispersion effects. Data collection was with Mo radiation and no heavy atoms are present. Chirality at each stereocenter was confirmed by comparison to the known stereochemistry of the commercially available material.

Hydrogen atoms were located from Fourier maps (Q-peaks) and all hydrogen atom parameters were refined.

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO* (Agilent, 2011); data reduction: *CrysAlis PRO* (Agilent, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

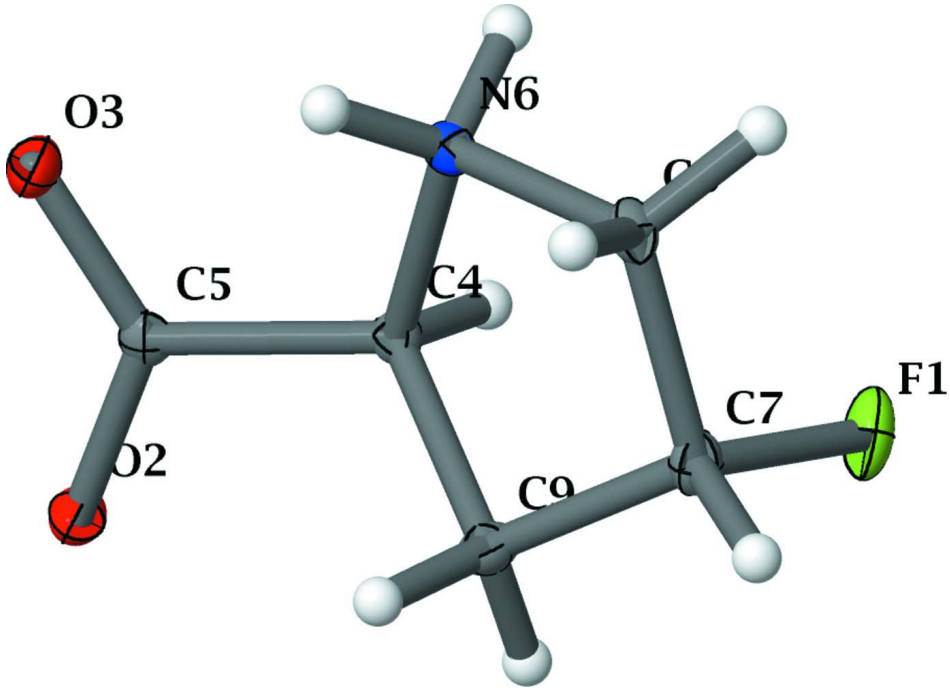


Figure 1

View of the title compound showing displacement ellipsoids at the 50% probability level.

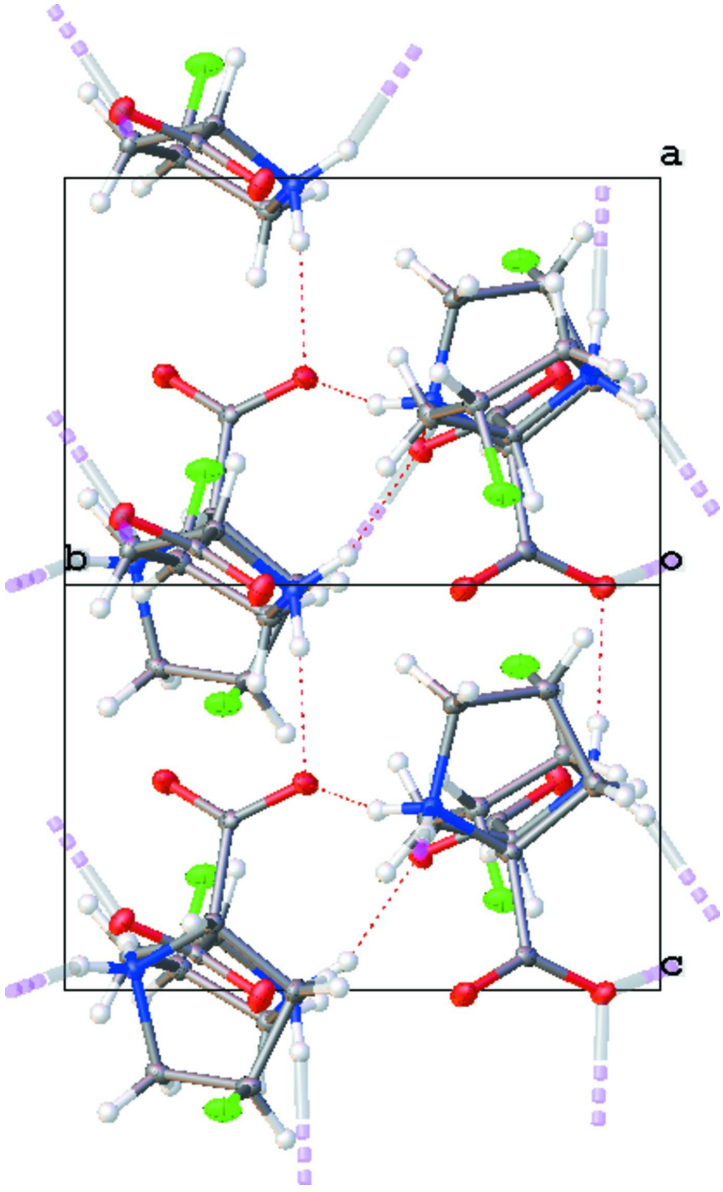


Figure 2

A view of a section of the crystal packing of the title compound along [101] showing N6–H6B···O2^{i} and N6–H6A···O2^{ii} hydrogen bonds [Symmetry code (i) 3/2 - *x*, 1 - *y*, 1/2 + *z*; (ii) +*x*, +*y*, 1 + *z*].

(2*S*,4*R*)-4-Fluoropyrrolidinium-2-carboxylate

Crystal data

$C_5H_8FNO_2$
M_r = 133.12
Orthorhombic, $P2_12_12_1$
a = 7.6530 (6) Å
b = 8.4128 (6) Å
c = 8.6286 (6) Å
V = 555.54 (7) Å^3
Z = 4
F(000) = 280

D_x = 1.592 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 1887 reflections
θ = 3.6–30.0°
μ = 0.14 mm^{-1}
T = 100 K
Prism, clear light colourless
0.26 × 0.05 × 0.03 mm

Data collection

Oxford Diffraction Gemini Ultra diffractometer
Radiation source: fine-focus sealed tube, fine-focus sealed tube
Graphite monochromator
Detector resolution: 16.0122 pixels mm^{-1}
phi and ω scans
Absorption correction: gaussian (*CrysAlis PRO*; Agilent, 2011)
T_{min} = 0.977, T_{max} = 0.996
10227 measured reflections
959 independent reflections
832 reflections with $I > 2\sigma(I)$
R_{int} = 0.082
θ_{max} = 30.1°, θ_{min} = 3.6°
h = −10→10
k = −11→11
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.073
S = 1.07
959 reflections
114 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0203P)^2 + 0.2288P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Special details

Experimental. Recrystallized from 50/50 acetone/water.
Absorption correction: CrysAlisPro, Agilent Technologies, Version 1.171.34.49 (release 20-01-2011 CrysAlis171 .NET) (compiled Jan 20 2011,15:58:25) Numerical absorption correction based on gaussian integration over a multifaceted crystal model
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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
F1	0.24111 (16)	0.73474 (16)	0.53792 (14)	0.0194 (3)
O2	0.58809 (19)	0.59578 (17)	0.07960 (17)	0.0143 (3)
O3	0.4982 (2)	0.82996 (18)	−0.01402 (17)	0.0177 (3)
N6	0.2662 (2)	0.8837 (2)	0.2162 (2)	0.0109 (3)
C4	0.3974 (3)	0.7510 (2)	0.2345 (2)	0.0104 (4)
C5	0.5019 (3)	0.7239 (2)	0.0854 (2)	0.0104 (4)
C7	0.1571 (3)	0.6913 (3)	0.3970 (2)	0.0130 (4)
C8	0.1078 (3)	0.8427 (3)	0.3133 (2)	0.0124 (4)
C9	0.2903 (3)	0.6117 (3)	0.2947 (2)	0.0137 (4)
H4	0.480 (3)	0.787 (3)	0.317 (3)	0.010 (6)*
H8A	0.011 (3)	0.822 (3)	0.247 (3)	0.013 (6)*
H7	0.056 (3)	0.629 (3)	0.424 (3)	0.011 (6)*
H8B	0.084 (3)	0.927 (3)	0.387 (3)	0.008 (6)*

H9A	0.233 (3)	0.560 (3)	0.208 (3)	0.020 (7)*
H9B	0.358 (3)	0.540 (3)	0.353 (3)	0.022 (7)*
H6A	0.231 (3)	0.895 (3)	0.115 (3)	0.026 (7)*
H6B	0.314 (3)	0.975 (3)	0.256 (3)	0.020 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0170 (6)	0.0320 (8)	0.0092 (6)	0.0011 (6)	0.0006 (5)	0.0004 (5)
O2	0.0151 (7)	0.0142 (7)	0.0136 (7)	0.0048 (6)	0.0027 (6)	0.0023 (6)
O3	0.0248 (8)	0.0158 (7)	0.0124 (7)	0.0051 (7)	0.0053 (7)	0.0031 (6)
N6	0.0115 (8)	0.0101 (8)	0.0112 (8)	0.0008 (7)	0.0000 (7)	−0.0014 (7)
C4	0.0110 (8)	0.0110 (9)	0.0091 (8)	0.0004 (8)	−0.0003 (7)	−0.0002 (8)
C5	0.0094 (8)	0.0113 (9)	0.0106 (8)	−0.0034 (8)	0.0000 (7)	−0.0015 (8)
C7	0.0119 (9)	0.0158 (10)	0.0114 (9)	−0.0018 (8)	0.0018 (8)	−0.0003 (8)
C8	0.0106 (9)	0.0153 (9)	0.0112 (9)	0.0017 (8)	0.0007 (8)	−0.0022 (8)
C9	0.0149 (10)	0.0118 (9)	0.0144 (10)	0.0009 (8)	0.0013 (8)	0.0035 (9)

Geometric parameters (Å, º)

F1—C7	1.423 (2)	C4—H4	1.00 (2)
O2—C5	1.265 (2)	C7—C8	1.512 (3)
O3—C5	1.238 (2)	C7—C9	1.505 (3)
N6—C4	1.509 (3)	C7—H7	0.96 (2)
N6—C8	1.513 (3)	C8—H8A	0.95 (3)
N6—H6A	0.91 (3)	C8—H8B	0.97 (2)
N6—H6B	0.92 (3)	C9—H9A	0.97 (3)
C4—C5	1.532 (3)	C9—H9B	0.94 (3)
C4—C9	1.521 (3)		
C4—N6—C8	107.85 (15)	F1—C7—H7	107.3 (14)
C4—N6—H6A	111.6 (17)	C8—C7—H7	111.6 (13)
C4—N6—H6B	108.2 (15)	C9—C7—C8	105.27 (17)
C8—N6—H6A	108.5 (17)	C9—C7—H7	116.6 (14)
C8—N6—H6B	107.5 (15)	N6—C8—H8A	109.4 (15)
H6A—N6—H6B	113 (2)	N6—C8—H8B	110.1 (13)
N6—C4—C5	111.70 (16)	C7—C8—N6	104.86 (16)
N6—C4—C9	104.28 (16)	C7—C8—H8A	109.3 (15)
N6—C4—H4	105.8 (13)	C7—C8—H8B	110.5 (13)
C5—C4—H4	108.2 (13)	H8A—C8—H8B	112.4 (19)
C9—C4—C5	116.93 (17)	C4—C9—H9A	108.9 (15)
C9—C4—H4	109.3 (13)	C4—C9—H9B	112.4 (15)
O2—C5—C4	115.64 (17)	C7—C9—C4	102.86 (17)
O3—C5—O2	126.79 (19)	C7—C9—H9A	110.3 (15)
O3—C5—C4	117.53 (18)	C7—C9—H9B	110.2 (15)
F1—C7—C8	107.72 (17)	H9A—C9—H9B	112 (2)
F1—C7—C9	108.03 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N6—H6*B*···O2^{i}	0.92 (3)	1.90 (3)	2.744 (2)	152 (2)
N6—H6*A*···O2^{ii}	0.91 (3)	2.01 (3)	2.899 (2)	164 (2)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) *x*−1/2, −*y*+3/2, −*z*.