Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Unconventional preparation of racemic crystals of isopropyl 3,3,3-trifluoro-2-hydroxypropanoate and their unusual crystallographic structure; the ultimate preference for homochiral intermolecular interactions

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Table 1 Some key crystallographic data for enantiomerically pure and racemic trifluorolactate **1**.

	Enantiomerically pure crystals	Racemic crystals
Crystal habit	Colorless needle	Colorless plate
Crystal system	Orthorhombic	Monoclinic
Space group	P212121	P21/n
Unit cell dimensions	a = 9.851(2) b = 16.372(1) c = 5.2625(3)	a = 12.110(3) b = 5.3559(12) c = 12.544(3)
Volume	848.77(8) $Å^3$	812.3(3) $Å^3$
Density	1.456 g/cm^3	1.522 g/cm^3
M.p.	79 ºC	57 ºC

Size-Exclusion Chromatography details

Size-Exclusion Chromatography (SEC) was conducted at ambient temperatures (17-23 °C), 8.0 mm x 500 mm polystyrene gel column (JAIGEL-2.5H-A) was used on JASCO 880-PU equipped with UV-Vis wavelength and CD JASCO detectors.

Small Molecule Crystallography Lab
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Sample: rac-CF3-CHOH-COOH Lab ID: 09014
User:
Formula: $C_6 H_9 F_3 O_3$
Date of submission: March 3, 2009

For Prof. Vadym Soloshonok

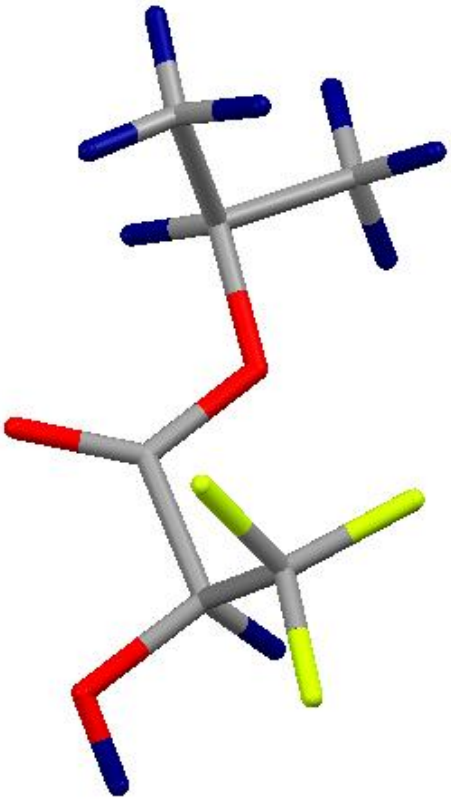

Figure 1

Comment

The intensity data were truncated at 0.87 Å resolution because data in higher resolution shells all had R(int) > 0.25. The compound crystallized as racemates. The displacement ellipsoids were drawn at the 50% probability level.

Experimental

A colorless plate-shaped crystal of dimensions 0.45 x 0.44 x 0.07 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX ccd area detector (1) and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The sample was cooled to 100(2) K. Cell parameters were determined from a non-linear least squares fit of 4058 peaks in the range 3.25 < θ < 28.34°. A total of 6123 data were measured in the range 2.27 < θ < 24.11° using ω oscillation frames. The data were corrected for absorption by the semi-empirical method (2) giving minimum and maximum transmission factors of 0.928 and 0.992. The data were merged to form a set of 1291 independent data with R(int) = 0.0546 and a coverage of 100.0 %.

The monoclinic space group $P2_1/n$ was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 (3). Hydrogen atom positions of hydrogens bonded to carbons were initially determined by geometry and refined by a riding model. The hydroxy hydrogen was located on a difference map, and its position was refined independently. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the displacement parameters of the bonded atoms. A total of 112 parameters were refined against 1291 data to give wR(F^2) = 0.2058 and S = 1.141 for weights of w = 1/[σ^2 (F^2) + (0.1040 P)^2 + 1.6000 P], where P = [F_o^2 + 2F_c^2] / 3. The final R(F) was 0.0612 for the 981 observed, [F > 4σ(F)], data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.437 and -0.298 e/Å^3, respectively.

Acknowledgment

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References

(1) (a) Data Collection: SMART Software Reference Manual (1998). Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA. (b) Data Reduction: SAINT Software Reference Manual (1998). Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

(2) G. M. Sheldrick (2007). SADABS. Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen, Germany.

(3) (a) G. M. Sheldrick (2008). *Acta Cryst. A64*, 112-122. (b) *International Tables for Crystallography, Vol C,* Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2, Kluwer: Boston (1995).

Table 2. Crystal data and structure refinement for 09014.

Empirical formula	$C_6 H_9 F_3 O_3$	
Formula weight	186.13	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.110(3) Å	α= 90°
	b = 5.3559(12) Å	β= 93.203(4)°
	c = 12.544(3) Å	γ= 90°
Volume	812.3(3) Å^3	
Z, Z'	4, 1	
Density (calculated)	1.522 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	384	
Absorption coefficient	0.161 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.992 and 0.928	
Theta range for data collection	2.27 to 24.11°	
Reflections collected	6123	
Independent reflections	1291 [R(int) = 0.0546]	
Data / restraints / parameters	1291 / 0 / 112	
$wR(F^2$ all data)	$wR2$ = 0.2058	
R(F obsd data)	$R1$ = 0.0612	
Goodness-of-fit on F^2	1.141	
Observed data [I > 2σ(I)]	981	
Largest and mean shift / s.u.	0.000and 0.000	
Largest diff. peak and hole	0.437 and -0.298 e/Å^3	

$wR2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Table 3. Atomic coordinates and equivalent isotropic displacement parameters for 09014. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	0.7143(4)	0.4142(9)	0.4773(4)	0.0327(11)
C(2)	0.6311(4)	0.2397(8)	0.4216(3)	0.0282(10)
C(3)	0.6832(4)	0.0521(8)	0.3511(4)	0.0370(12)
O(4)	0.5571(2)	0.4067(5)	0.3549(2)	0.0275(8)
C(5)	0.4589(3)	0.3161(8)	0.3218(3)	0.0238(10)
O(6)	0.4229(2)	0.1132(5)	0.3424(2)	0.0291(8)
C(7)	0.3945(3)	0.5073(8)	0.2535(3)	0.0252(10)
O(8)	0.2872(2)	0.4135(6)	0.2329(2)	0.0287(8)
C(9)	0.4472(4)	0.5476(8)	0.1480(4)	0.0303(11)
F(10)	0.3804(2)	0.6810(5)	0.0810(2)	0.0408(8)
F(11)	0.5428(2)	0.6714(5)	0.1595(2)	0.0404(8)
F(12)	0.4673(2)	0.3328(5)	0.0996(2)	0.0420(8)

Table 4. Bond lengths [Å] and angles [°] for 09014.

C(1)-C(2)	1.516(6)	O(4)-C(5)	1.329(5)
C(1)-H(1A)	0.9800	C(5)-O(6)	1.204(5)
C(1)-H(1B)	0.9800	C(5)-C(7)	1.522(6)
C(1)-H(1C)	0.9800	C(7)-O(8)	1.404(5)
C(2)-O(4)	1.490(5)	C(7)-C(9)	1.516(6)
C(2)-C(3)	1.500(7)	C(7)-H(7)	1.0000
C(2)-H(2)	1.0000	O(8)-H(8)	0.90(5)
C(3)-H(3A)	0.9800	C(9)-F(12)	1.329(5)
C(3)-H(3B)	0.9800	C(9)-F(11)	1.334(5)
C(3)-H(3C)	0.9800	C(9)-F(10)	1.340(5)
C(2)-C(1)-H(1A)	109.5	C(5)-O(4)-C(2)	117.1(3)
C(2)-C(1)-H(1B)	109.5	O(6)-C(5)-O(4)	126.2(4)
H(1A)-C(1)-H(1B)	109.5	O(6)-C(5)-C(7)	123.3(4)
C(2)-C(1)-H(1C)	109.5	O(4)-C(5)-C(7)	110.6(3)
H(1A)-C(1)-H(1C)	109.5	O(8)-C(7)-C(9)	108.7(3)
H(1B)-C(1)-H(1C)	109.5	O(8)-C(7)-C(5)	107.6(3)
O(4)-C(2)-C(3)	109.3(3)	C(9)-C(7)-C(5)	111.1(4)
O(4)-C(2)-C(1)	104.6(3)	O(8)-C(7)-H(7)	109.8
C(3)-C(2)-C(1)	113.2(4)	C(9)-C(7)-H(7)	109.8
O(4)-C(2)-H(2)	109.8	C(5)-C(7)-H(7)	109.8
C(3)-C(2)-H(2)	109.8	C(7)-O(8)-H(8)	104(3)
C(1)-C(2)-H(2)	109.8	F(12)-C(9)-F(11)	107.4(4)
C(2)-C(3)-H(3A)	109.5	F(12)-C(9)-F(10)	107.1(3)
C(2)-C(3)-H(3B)	109.5	F(11)-C(9)-F(10)	107.0(4)
H(3A)-C(3)-H(3B)	109.5	F(12)-C(9)-C(7)	111.8(4)
C(2)-C(3)-H(3C)	109.5	F(11)-C(9)-C(7)	112.4(3)
H(3A)-C(3)-H(3C)	109.5	F(10)-C(9)-C(7)	110.8(4)
H(3B)-C(3)-H(3C)	109.5		

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 09014. The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	31(3)	35(3)	30(2)	-1(2)	-19(2)	1(2)
C(2)	26(2)	27(2)	29(2)	8(2)	-18(2)	0(2)
C(3)	33(3)	30(3)	46(3)	-2(2)	-17(2)	-1(2)
O(4)	24(2)	28(2)	29(2)	4(1)	-17(1)	-1(1)
C(5)	23(2)	26(2)	21(2)	-3(2)	-9(2)	-1(2)
O(6)	27(2)	26(2)	33(2)	2(1)	-12(1)	-3(1)
C(7)	19(2)	27(2)	29(2)	-2(2)	-12(2)	-2(2)
O(8)	20(2)	28(2)	37(2)	1(1)	-14(1)	1(1)
C(9)	26(2)	30(2)	34(2)	1(2)	-13(2)	-2(2)
F(10)	34(2)	56(2)	31(1)	14(1)	-16(1)	6(1)
F(11)	29(2)	55(2)	35(2)	10(1)	-12(1)	-11(1)
F(12)	44(2)	49(2)	32(2)	-6(1)	-5(1)	5(1)

Table 6. Hydrogen coordinates and isotropic displacement parameters for 09014.

	x	y	z	U(eq)
H(1A)	0.7587	0.3215	0.5318	0.049
H(1B)	0.6751	0.5502	0.5113	0.049
H(1C)	0.7630	0.4837	0.4249	0.049
H(2)	0.5876	0.1518	0.4756	0.034
H(3A)	0.7232	0.1393	0.2964	0.056
H(3B)	0.6255	-0.0532	0.3165	0.056
H(3C)	0.7349	-0.0525	0.3943	0.056
H(7)	0.3912	0.6692	0.2929	0.030
H(8)	0.244(4)	0.550(9)	0.229(4)	0.034

Table 7. Torsion angles [°] for 09014.

C(3)-C(2)-O(4)-C(5)	77.5(5)
C(1)-C(2)-O(4)-C(5)	-160.9(4)
C(2)-O(4)-C(5)-O(6)	1.7(6)
C(2)-O(4)-C(5)-C(7)	-179.0(3)
O(6)-C(5)-C(7)-O(8)	6.9(6)
O(4)-C(5)-C(7)-O(8)	-172.5(3)
O(6)-C(5)-C(7)-C(9)	-112.1(5)
O(4)-C(5)-C(7)-C(9)	68.6(4)
O(8)-C(7)-C(9)-F(12)	-68.5(4)
C(5)-C(7)-C(9)-F(12)	49.7(4)
O(8)-C(7)-C(9)-F(11)	170.5(3)
C(5)-C(7)-C(9)-F(11)	-71.2(5)
O(8)-C(7)-C(9)-F(10)	50.9(5)
C(5)-C(7)-C(9)-F(10)	169.1(3)

Table 8. Hydrogen bonds for 09014[Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(8)-H(8)...O(8)#1	0.90(5)	2.05(5)	2.865(2)	151(4)
O(8)-H(8)...O(6)#1	0.90(5)	2.19(5)	2.871(4)	132(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+1/2