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## Key indicators

Single-crystal X-ray study  
 $T = 303$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å  
 $R$  factor = 0.073  
 $wR$  factor = 0.188  
Data-to-parameter ratio = 18.1For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.3-*trans*-Bromo-5-*cis*-fluoro-2,6,6-trimethyl-2-phenyl-  
tetrahydropyran

The title compound,  $\text{C}_{14}\text{H}_{18}\text{BrFO}$ , is a hexasubstituted tetrahydropyran with two halogen atoms attached in  $\beta$  and four C substituents in  $\alpha$  positions with respect to the ether O atom. The C...C distance [3.183 (7) Å] between the two 1,3-diaxially oriented  $\alpha$ -methyl groups falls below the sum of the van der Waals radii. The magnitude of the bond angle at oxygen [122.6 (3)°] and a comparatively small displacement of this atom [0.490 (5) Å] from the mean plane of four C atoms of the tetrahydropyran ring indicate a marked flattening of the heterocyclic ring in its  ${}^1\text{C}_4$  conformation.

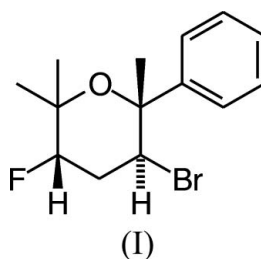
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## Comment

Atoms C2, C3 and C5 in the title compound, (I), are stereogenic centers. The racemate of (I) was prepared in the course of a study directed toward the synthesis of hitherto unknown analogues of the marine natural product aplysiapyranoid A (Hartung & Greb, 2003; Hartung, Greb *et al.*, 2005). The solid-state geometry of (I) was investigated by X-ray diffraction in order to uncover the effects of 2,6-diaxial substitution on the geometry of substituted tetrahydropyrans.



Atoms O1 and C4 are displaced in opposite directions [−0.490 (5) and 0.673 (7) Å, respectively] from the mean plane formed by atoms C2/C3/C5/C6 [the deviation of C6 is −0.09 (1) Å] (Fig. 1). This arrangement ( ${}^1\text{C}_4$ ) corresponds to the most highly populated conformer of (I) in  $\text{CDCl}_3$  solution, as derived from the magnitude of the vicinal proton-proton coupling constants ( ${}^1\text{H}$  NMR). The interplanar angle between the segments C2/O1/C6 and C2/C3/C5/C6 is 44.7 (3)°, which is smaller than the inclination between the planes C3/C4/C5 and C2/C3/C5/C6 [50.0 (3)°]. The plane of the equatorially positioned 2-phenyl group is aligned approximately in eclipsic arrangement with respect to C9 [C11–C10–C2–C9 = 11.0 (6)°]. The distance C7...C9 of 3.183 (7) Å is smaller than the sum of the van der Waals radii (1.70 Å; Bondi, 1964). The large endocyclic bond angle C2–O1–C6 of 122.6 (3)° and the comparatively small value of 309° for the sum of the absolute values of the six endocyclic torsion angles indicate a flattening of the tetrahydropyran ring, in particular at oxygen (Hartung,

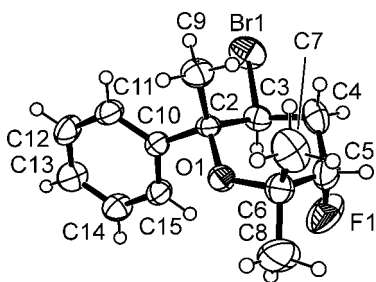


Figure 1

The molecular structure of (I). Displacement ellipsoids are plotted at the 50% probability level.

Svoboda, Schmidt & Murso, 2005; Hartung, Svoboda, Schmidt & Pfeiffer, 2005) (Table 1). The bond lengths C3—Br1 [1.963 (4) Å] and C5—F1 [1.400 (6) Å] are in agreement with the reported mean values for Br—Csp<sup>3</sup> [1.97 (3) Å] and Csp<sup>3</sup>—F bonds [1.40 (2) Å] (Allen *et al.*, 1987).

## Experimental

The title compound, (I), was prepared by treatment of a solution of racemic 5-bromo-2,2,6-trimethyl-6-phenyltetrahydropyran-2-carboxylic acid (245 mg, 0.75 mmol; Hartung & Greb, 2003) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (10 ml) with XeF<sub>2</sub> (181 mg, 1.06 mmol) (Hartung, Greb *et al.*, 2005). The reaction mixture was stirred for 18 h at 293 K. Afterwards, it was washed with an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (5 ml, 5% w/w). The organic phase was dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to provide an oil, which was purified by chromatography [SiO<sub>2</sub>, petroleum ether/diethyl ether = 10:1 (v/v)] to afford 76.8 mg (34%) of a 30:70 mixture of 3-*trans*-bromo-5-*trans*-fluoro-2,6,6-trimethyl-2-phenyltetrahydropyran (*R*<sub>F</sub> = 0.71) and (I) (*R*<sub>F</sub> = 0.62) as a colorless oil. Rod-shaped crystals of (I) suitable for X-ray diffraction were obtained by slow evaporation of a solution of the diastereomers in petroleum ether/diethyl ether. Analysis calculated for C<sub>14</sub>H<sub>18</sub>BrFO: C 55.83, H 6.02%; found C 55.38, H 5.88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.29 (*d*, <sup>4</sup>*J*<sub>HF</sub> = 3.3 Hz, 3H), 1.42 (*d*, <sup>4</sup>*J*<sub>HF</sub> = 1.3 Hz, 3H), 1.84 (*s*, 3H), 2.58–2.73 (*m*, 2H), 4.49 (*dt*, <sup>2</sup>*J*<sub>d,HF</sub> = 49.0 Hz, <sup>3</sup>*J*<sub>F</sub> = 3.5 Hz, 1H), 4.55 (*m*, 1H), 7.27–7.37 (*m*, 3H), 7.59–7.63 (*m*, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz): 22.7, 26.4 (*d*, <sup>3</sup>*J*<sub>CF</sub> = 9.6 Hz), 27.2 (*d*, <sup>3</sup>*J*<sub>CF</sub> = 5.4 Hz), 33.9 (*d*, <sup>2</sup>*J*<sub>CF</sub> = 21.9 Hz), 53.4 (*d*, <sup>3</sup>*J*<sub>CF</sub> = 3.8 Hz), 74.7 (*d*, <sup>2</sup>*J*<sub>CF</sub> = 19.2 Hz), 78.0, 92.7 (*d*, <sup>1</sup>*J*<sub>CF</sub> = 180 Hz), 126.2, 127.6, 145.4.

### Crystal data

C <sub>14</sub> H <sub>18</sub> BrFO	Mo Kα radiation
<i>M</i> <sub>r</sub> = 301.19	Cell parameters from 2925 reflections
Orthorhombic, <i>Pbca</i>	<i>θ</i> = 2.8–21.8°
<i>a</i> = 9.410 (1) Å	<i>μ</i> = 2.98 mm <sup>-1</sup>
<i>b</i> = 12.605 (1) Å	<i>T</i> = 303 (2) K
<i>c</i> = 23.229 (2) Å	Rod, colorless
<i>V</i> = 2755.3 (4) Å <sup>3</sup>	0.76 × 0.16 × 0.16 mm
<i>Z</i> = 8	
<i>D</i> <sub>x</sub> = 1.452 Mg m <sup>-3</sup>	

### Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector	16564 measured reflections
<i>ω</i> scans	2809 independent reflections
Absorption correction: analytical (CrysAlis RED; Oxford Diffraction, 2002)	1991 reflections with <i>I</i> > 2σ( <i>I</i> )
<i>T</i> <sub>min</sub> = 0.312, <i>T</i> <sub>max</sub> = 0.717	<i>R</i> <sub>int</sub> = 0.082
	<i>θ</i> <sub>max</sub> = 26.4°
	<i>h</i> = -11 → 11
	<i>k</i> = -15 → 9
	<i>l</i> = -29 → 29

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.073  
*wR*(*F*<sup>2</sup>) = 0.188  
*S* = 1.20  
 2809 reflections  
 155 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.079P)^2 + 0.7239P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.015$   
 $\Delta\rho_{\max} = 0.74 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.66 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C2—O1	1.452 (5)	C4—C5	1.496 (7)
C2—C9	1.521 (6)	C5—C6	1.516 (7)
C2—C10	1.527 (6)	C6—O1	1.452 (5)
C2—C3	1.541 (5)	C6—C8	1.501 (7)
C3—C4	1.512 (6)	C6—C7	1.545 (7)
O1—C2—C3	106.3 (3)	C4—C5—C6	113.9 (4)
C4—C3—C2	113.5 (4)	O1—C6—C5	109.9 (4)
C5—C4—C3	108.6 (4)	C6—O1—C2	122.6 (3)
O1—C2—C3—C4	-52.9 (5)	C4—C5—C6—O1	47.1 (6)
C9—C2—C3—C4	69.0 (5)	C4—C5—C6—C7	-76.7 (5)
C10—C2—C3—C4	-163.2 (4)	C9—C2—C10—C11	11.0 (6)
C2—C3—C4—C5	58.7 (5)	C8—C6—O1—C2	-167.4 (5)
Br1—C3—C4—C5	-177.1 (3)	C5—C6—O1—C2	-46.6 (5)
C3—C4—C5—F1	65.5 (5)	C3—C2—O1—C6	48.7 (5)
C3—C4—C5—C6	-54.8 (6)		

All H atoms were positioned geometrically and treated as riding atoms (C—H = 0.93–0.98 Å), with the *U*<sub>iso</sub>(H) values set at 1.2*U*<sub>eq</sub> of the parent atom.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON2002* (Spek, 2003) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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