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Homochiral Methyl (*S*)-2-Benzoyloxy-4-bromo-4-methylpentanoate

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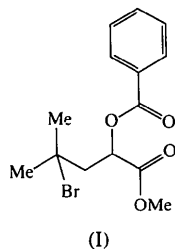
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Abstract

The stereochemistry at position 2 of the title compound, $C_{14}H_{17}BrO_4$, has been confirmed as *S*.

Comment

The title compound, methyl (*S*)-2-benzoyloxy-4-bromo-4-methylpentanoate, (I), was investigated as part of a study of the regioselective bromination of 2-hydroxy-4-methylpentanoic acid derivatives (Shaw, Tan & Blackman, 1995). X-ray structure analysis was undertaken in order to confirm that the stereochemistry at the 2 position (*i.e.* atom C5) was unaffected by the bromination reaction.



The compound crystallized as large blocks; the smallest of these was used for data collection as, despite repeated attempts, suitable smaller crystals could not be obtained. Cutting the crystal also destroyed the crystal

mosaicity. Despite the fact that there may have been some reflections for which the crystal was not bathed in a uniform beam, the quality of the data does not appear to have been affected, as evidenced by the excellent results. We have previously used similarly large crystals without deleterious effects (Shaw, Tan & Blackman, 1995).

Refinement in the orthorhombic space group $P2_12_12_1$ showed the presence of only one enantiomer. The stereochemistry at atom C5 was found to be *S*, with the correct choice of 'handedness' verified by the value of the Flack (1983) parameter [$\chi = -0.01(2)$]. All bond lengths and angles within the identical fragments of (I) and methyl (*S*)-2-benzoyloxy-4-bromo-4-methylpentanoate are the same within three e.s.d.'s, with the exception of the O3—C5—C7 angle [107.2(3) versus 111.6(4)° in the latter] (Shaw, Tan & Blackman, 1995).

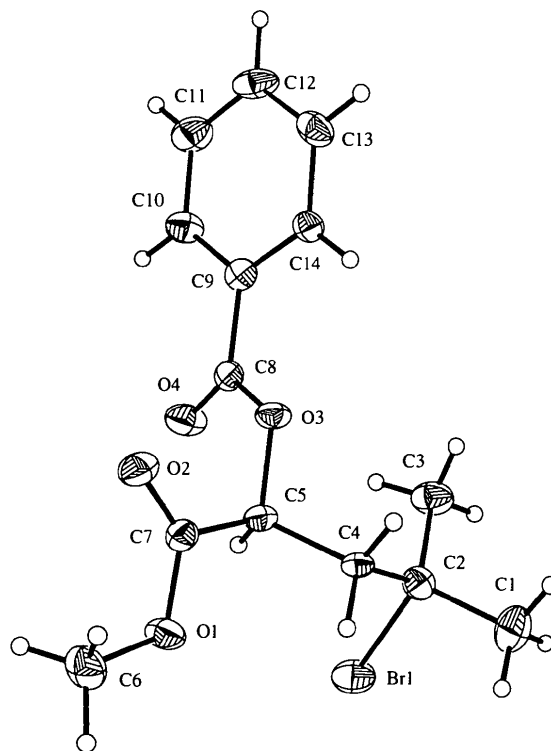


Fig. 1. ORTEP (Johnson, 1965) drawing of (I) showing displacement ellipsoids at the 50% probability level.

Experimental

A mixture of methyl (*S*)-2-benzoyloxy-4-methylpentanoate (1.11 g, 4.4 mmol) and *N*-bromosuccinimide (1.18 g, 6.6 mmol) in benzene (100 ml) was heated at reflux under

nitrogen for 14 h, with reaction initiated by irradiation with a 160 W mercury lamp. The reaction mixture was then cooled, filtered and evaporated under reduced pressure. The residue was column chromatographed on silica with hexane/ethyl acetate (3:1) and the product was recrystallized from dichloromethane and hexane (Shaw & Tan, 1995).

Crystal data

C ₁₄ H ₁₇ BrO ₄	Mo K α radiation
$M_r = 329.19$	$\lambda = 0.7107 \text{ \AA}$
Orthorhombic	Cell parameters from 25
$P2_12_12_1$	reflections
$a = 8.281 (2) \text{ \AA}$	$\theta = 8\text{--}13^\circ$
$b = 12.084 (3) \text{ \AA}$	$\mu = 2.842 \text{ mm}^{-1}$
$c = 14.491 (5) \text{ \AA}$	$T = 130 (2) \text{ K}$
$V = 1450.1 (7) \text{ \AA}^3$	Block
$Z = 4$	$0.96 \times 0.82 \times 0.68 \text{ mm}$
$D_x = 1.508 \text{ Mg m}^{-3}$	Colourless

Data collection

Nicolet R3m diffractometer	$R_{\text{int}} = 0.025$
ω scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction:	$h = 0 \rightarrow 10$
ψ scans	$k = -1 \rightarrow 15$
$T_{\text{min}} = 0.363$, $T_{\text{max}} = 0.805$	$l = -18 \rightarrow 18$
2248 measured reflections	3 standard reflections
2155 independent reflections	monitored every 97
1854 observed reflections	reflections
$[I > 2\sigma(I)]$	intensity decay: 2%

Refinement

Refinement on F^2	$\Delta\rho_{\text{max}} = 0.425 \text{ e \AA}^{-3}$
$R(F) = 0.0418$	$\Delta\rho_{\text{min}} = -0.680 \text{ e \AA}^{-3}$
$wR(F^2) = 0.0930$	Atomic scattering factors
$S = 1.054$	from <i>International Tables</i>
2155 reflections	for <i>Crystallography</i> (1992,
175 parameters	Vol. C, Tables 4.2.6.8 and
Only coordinates of H atoms	6.1.1.4)
refined	Absolute configuration:
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2]$	Flack (1983) parameter
where $P = (F_o^2 + 2F_c^2)/3$	$= -0.01 (2)$
$(\Delta/\sigma)_{\text{max}} = 0.004$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	x	y	z	U_{eq}
Br1	0.04656 (6)	0.85201 (5)	0.31275 (3)	0.03249 (15)
C1	0.2572 (6)	0.8051 (5)	0.1644 (4)	0.0357 (13)
C2	0.0852 (5)	0.7768 (4)	0.1915 (3)	0.0234 (9)
C3	0.0627 (6)	0.6531 (4)	0.2078 (3)	0.0317 (11)
C4	-0.0316 (5)	0.8275 (3)	0.1222 (3)	0.0184 (9)
C5	-0.2110 (5)	0.8060 (4)	0.1412 (3)	0.0193 (9)
C6	-0.3813 (6)	1.0823 (4)	0.0874 (4)	0.0311 (12)
C7	-0.3209 (5)	0.8911 (4)	0.0946 (3)	0.0211 (10)
C8	-0.3524 (5)	0.6347 (4)	0.1558 (3)	0.0192 (9)
C9	-0.3974 (5)	0.5318 (4)	0.1075 (3)	0.0200 (10)
C10	-0.5263 (6)	0.4717 (4)	0.1416 (3)	0.0270 (10)
C11	-0.5743 (6)	0.3754 (4)	0.0975 (4)	0.0334 (12)
C12	-0.4941 (6)	0.3407 (4)	0.0186 (3)	0.0313 (12)
C13	-0.3652 (6)	0.4003 (4)	-0.0150 (3)	0.0283 (11)

C14	-0.3152 (5)	0.4961 (4)	0.0293 (3)	0.0208 (10)
O1	-0.2872 (4)	0.9917 (3)	0.1263 (2)	0.0267 (8)
O2	-0.4216 (3)	0.8699 (3)	0.0385 (2)	0.0307 (8)
O3	-0.2540 (4)	0.6990 (3)	0.1051 (2)	0.0221 (7)
O4	-0.3989 (4)	0.6614 (3)	0.2323 (2)	0.0324 (8)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Br1—C2	2.003 (5)	C8—O4	1.217 (5)
C1—C2	1.517 (6)	C8—O3	1.345 (5)
C2—C4	1.523 (6)	C8—C9	1.475 (7)
C2—C3	1.526 (7)	C9—C10	1.383 (6)
C4—C5	1.534 (5)	C9—C14	1.390 (6)
C5—O3	1.439 (6)	C10—C11	1.386 (7)
C5—C7	1.530 (7)	C11—C12	1.387 (7)
C6—O1	1.457 (5)	C12—C13	1.377 (7)
C7—O2	1.193 (5)	C13—C14	1.387 (7)
C7—O1	1.330 (6)		
C1—C2—C4	109.6 (4)	O4—C8—O3	122.5 (5)
C1—C2—C3	112.0 (4)	O4—C8—C9	125.2 (4)
C4—C2—C3	114.8 (4)	O3—C8—C9	112.3 (4)
C1—C2—Br1	106.0 (3)	C10—C9—C14	120.4 (4)
C4—C2—Br1	107.1 (3)	C10—C9—C8	117.9 (4)
C3—C2—Br1	106.8 (3)	C14—C9—C8	121.7 (4)
C2—C4—C5	115.4 (4)	C9—C10—C11	119.8 (5)
O3—C5—C7	107.2 (3)	C10—C11—C12	119.8 (5)
O3—C5—C4	109.1 (4)	C13—C12—C11	120.3 (5)
C7—C5—C4	112.5 (4)	C12—C13—C14	120.3 (5)
O2—C7—O1	125.3 (4)	C13—C14—C9	119.3 (4)
O2—C7—C5	124.9 (5)	C7—O1—C6	116.2 (4)
O1—C7—C5	109.7 (4)	C8—O3—C5	118.0 (4)

Data collection: *SHELXTL-Plus* (Sheldrick, 1990). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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