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Benzyl 5-bromo-4-methylsalicylate

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Key indicators

Single-crystal X-ray study
T = 566 K
Mean σ(C–C) = 0.006 Å
R factor = 0.044
wR factor = 0.106
Data-to-parameter ratio = 13.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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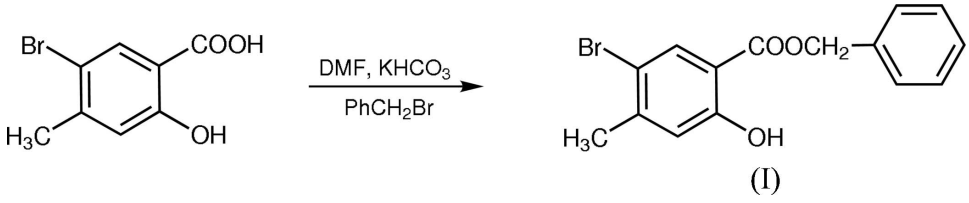
The title compound, $C_{15}H_{13}BrO_3$, was synthesized by the benzyl esterification of 5-bromo-4-methylsalicylic acid. The molecular conformation is stabilized by an intramolecular hydrogen bond.

Comment

Phenolic acid ester motifs have been found in many bioactive natural products, for example, the NF-$_\kappa$B inhibitors CAPE (Natarajan *et al.*, 1996) and the honeybee propolis contact allergen prenyl caffeate (Stüwe *et al.*, 1989). Moreover, phenolic acid esters are also used as important intermediates for the synthesis of medicines (Rotella *et al.*, 2000; Xu *et al.*, 2002). Recently, we reported a reaction to provide a clean practical method for efficient and chemoselective esterification of phenolic acids in high yields (Guo *et al.*, 2005). The title compound, (I), is an example obtained through this method. The molecular conformation of (I) is illustrated in Fig. 1. There is an intramolecular hydrogen bond in the crystal structure. The dihedral angle between the two benzene rings is 86.26 (9)°. Some geometric parameters are listed in Table 1 and a packing diagram is shown in Fig. 2.



(I)

Experimental

5-Bromo-4-methylsalicylic acid (2 mmol) was dissolved in dry dimethylformamide (3.0 ml); $KHCO_3$ (2.4 mmol) was added and the mixture was stirred for several minutes at room temperature. 1-(Bromomethyl)benzene (3 mmol) was then added. The reaction mixture was warmed to 313 K with a water bath and monitored by thin-layer column chromatography. Upon completion of the reaction, water (10 ml) was added and the mixture was extracted with ethyl acetate. The organic layer was subsequently washed with 5% $NaHCO_3$ and 5% NaCl, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and the excess of benzyl bromide was removed by column chromatography (EtOAc–hexane, 1:10). The product was dissolved in ethyl acetate and petroleum ether, and the solution was set aside at room temperature. As the solvent evaporated, crystals of (I) formed.

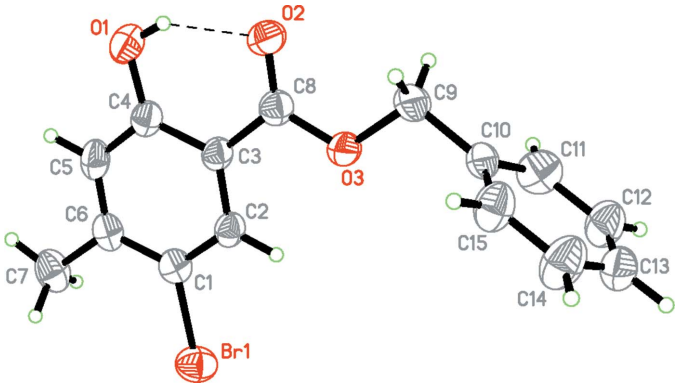


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids. The dashed line indicates a hydrogen bond.

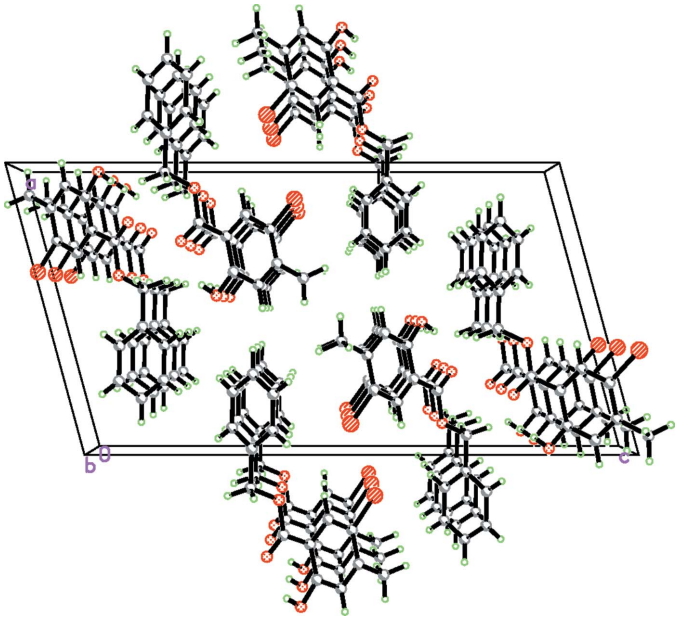


Figure 2
The packing viewed down the *b* axis.

Crystal data

$C_{15}H_{13}BrO_3$
M_r = 321.16
Monoclinic, $P2_1/n$
a = 12.242 (6) Å
b = 5.177 (3) Å
c = 22.376 (11) Å
β = 105.181 (7)°
V = 1368.6 (12) Å^3
Z = 4
D_x = 1.559 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1386 reflections
θ = 2.2–20.4°
μ = 3.00 mm^{-1}
T = 566 (2) K
Block, colourless
0.20 × 0.20 × 0.10 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.585, T_{max} = 0.753
6273 measured reflections
2406 independent reflections
1694 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 25.0°
$h = -14 \rightarrow 14$
$k = -4 \rightarrow 6$
$l = -26 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.106
S = 1.03
2406 reflections
174 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.0554P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C1	1.900 (4)	O3—C9	1.473 (4)
O1—C4	1.355 (4)	C6—C7	1.510 (5)
O2—C8	1.215 (4)	C9—C10	1.485 (5)
O3—C8	1.335 (4)		
Br1—C1—C6—C7	−0.6 (5)	C4—C3—C8—O3	−179.1 (3)
C9—O3—C8—O2	−3.2 (5)	O3—C9—C10—C11	92.2 (4)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.82	1.87	2.593 (4)	146

H atoms were placed in geometrically idealized positions, with Csp^3—H = 0.97 Å, Csp^2—H = 0.93 Å and O—H = 0.82 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(C,O)$ for methyl and OH groups, and $U_{iso}(H) = 1.2U_{eq}(C)$ for the remaining H atoms. The methyl group and the OH group were allowed to rotate but not to tip.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2000); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

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