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4-Bromo-2-(hydroxymethyl)phenol: helical hydrogen bonding, $R_2^2(12)$ rings and C—H$\cdots\pi$ interactions

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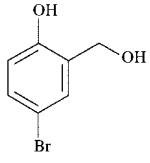
Apart from the O and H atoms of the hydroxymethyl group, molecules of the title compound, $C_7H_7BrO_2$, are essentially planar. Both O atoms act as hydrogen-bond donors and acceptors, resulting in helical hydrogen bonding in the direction of the *b* axis and the formation of $R_2^2(12)$ rings. Weaker C—H$\cdots\pi$ interactions are also present.

Comment

Many bromophenols have been detected in blood (Olsen *et al.*, 2002) and several antibacterial bromophenols are found in marine algae (Flodin & Whitfield, 1999). 4-Bromo-2-(hydroxymethyl)phenol (also known as 5-bromo-2-hydroxybenzyl alcohol or bromosaligenin) is an anti-inflammatory agent (Merck, 1989) and spasmolytic (Negwer, 2000). When two OH groups are present in a molecule, a variety of hydrogen-bonding patterns are possible (Brock, 2002), so the main interest in the solid-state structure of the title compound, (I), is the determination of the hydrogen-bonding motifs.



(I)

A view of the molecule is shown in Fig. 1. The out-of-plane O2 atom is 1.330 (3) Å from the mean plane of the remaining non-H atoms in the molecule, as indicated by the C1—C2—C7—O2 torsion angle [72.5 (3)°; Table 1]. There is no intramolecular hydrogen bonding between the two O atoms.

There are two intermolecular O—H$\cdots$O hydrogen bonds (Table 2) and, in both cases, the intermolecular O$\cdots$O separations [2.642 (3) and 2.781 (3) Å] are shorter than the corresponding intramolecular separation [3.086 (3) Å]. The hydrogen bonding is maximized by both O atoms acting as hydrogen-bond donors and acceptors, which results in an unusual three-dimensional pattern of hydrogen bonds. Fig. 2

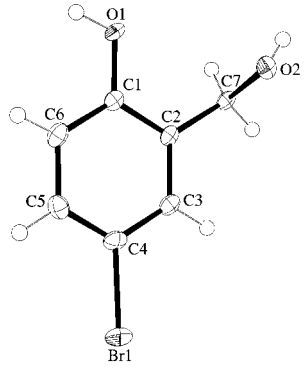


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

shows the continuous corkscrew or helical arrangement of hydrogen bonds along the *b* axis, with each helix involving all four symmetry-related molecules in the unit cell. The formation of the helices depends on the intermolecular symmetries [*i.e.* $(x, -y-\frac{1}{2}, z+\frac{1}{2})$ and $(1-x, -y, 2-z)$] of the hydrogen bonds, and both left- (L) and right-handed (R) helices are present in the lattice. The pitch of the helix equates to the length of the *b* axis [5.3329 (2) Å], and overall each molecule

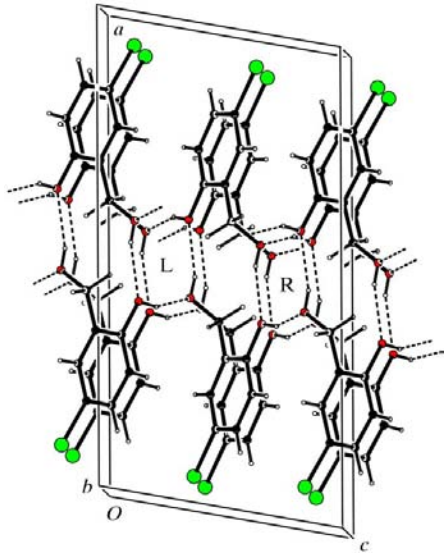


Figure 2
A view of the molecular packing of (I), showing the formation of left- (L) and right-handed (R) helical hydrogen bonds, and also $R_2^2(12)$ rings.

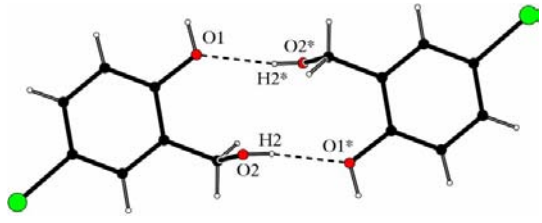


Figure 3
The formation of an $R_2^2(12)$ ring through intermolecular hydrogen bonding in (I). Atoms marked with an asterisk (*) are at the symmetry position $(1-x, -y, 2-z)$.

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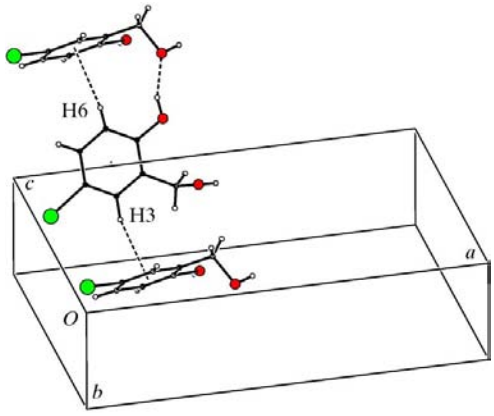

Figure 4
Part of the crystal structure of (I), showing the C—H···π interactions.

is linked to three other molecules by four classical hydrogen bonds. Fig. 3 shows that the hydrogen bonding also produces an $R_2^2(12)$ ring between two molecules. This dimer formation, also shown in Fig. 2, is across an inversion centre. In addition, there are weak intermolecular C—H···π interactions (Desiraju & Steiner, 1999), as shown in Fig. 4 and Table 2, but there is no evidence of any aromatic π–π interactions. The shortest Br···Br intermolecular separation is 3.7173 (1) Å, which is comparable to the sum of the van der Waals radii (3.70 Å; Bondi, 1964). The crystal structure of the related saligenin ($C_7H_8O_2$) molecule is also known (Zorkii *et al.*, 1985), but no atomic coordinates are available.

Experimental

The title compound was purchased from Sigma and recrystallized from diethyl ether.

Crystal data

$C_7H_7BrO_2$
M_r = 203.04
Monoclinic, $P2_1/c$
a = 16.3632 (5) Å
b = 5.3329 (2) Å
c = 8.4108 (3) Å
β = 100.364 (2)°
V = 721.98 (4) Å^3
Z = 4
D_x = 1.868 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3029 reflections
θ = 2.9–27.5°
μ = 5.62 mm^{-1}
T = 120 (2) K
Rod, colourless
0.40 × 0.24 × 0.18 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans to fill Ewald sphere
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.212, T_{max} = 0.431
5019 measured reflections
1614 independent reflections
1430 reflections with $I > 2\sigma(I)$
R_{int} = 0.067
θ_{max} = 27.5°
$h = -20 \rightarrow 20$
$k = -6 \rightarrow 6$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.114
S = 1.04
1614 reflections
119 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.074P)^2 + 0.392P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.17 e Å^{-3}
$\Delta\rho_{min}$ = −1.39 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C4	1.897 (3)	O2—C7	1.441 (3)
O1—C1	1.369 (3)	C2—C7	1.494 (4)
C3—C2—C7—O2	−106.5 (3)	C1—C2—C7—O2	72.5 (3)

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

Cg is the centre of gravity of the aryl ring.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{i}	0.88 (4)	1.81 (4)	2.642 (3)	159 (3)
O2—H2···O1^{ii}	0.77 (3)	2.04 (3)	2.781 (3)	162 (4)
C3—H3···*Cg*^{iii}	0.97 (3)	2.97 (3)	3.768 (3)	141 (3)
C6—H6···*Cg*^{iv}	0.88 (4)	2.97 (3)	3.717 (3)	144 (3)

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

H atoms were refined freely, with isotropic displacement parameters. The highest residual electron density in the final difference map was associated with atom Br1.

Data collection, cell refinement and data reduction: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); structure solution: *SIR*97 (Altomare *et al.*, 1999); structure refinement: *SHELXL*97 (Sheldrick, 1998); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1532). Services for accessing these data are described at the back of the journal.

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