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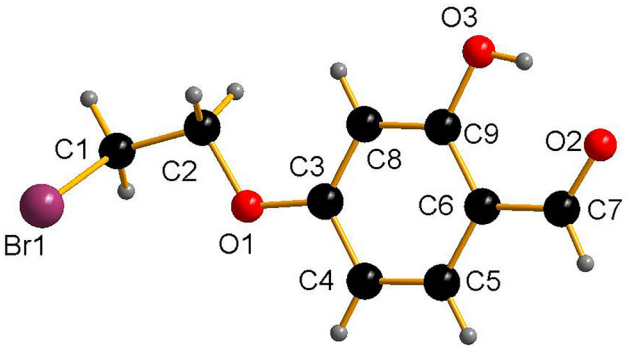
The crystal structure of 4-(2-bromoethoxy)-2-hydroxybenzaldehyde, $C_9H_9BrO_3$



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Abstract

$C_9H_9BrO_3$, monoclinic, $P2_1n$ (no. 14), a = 10.8914(4) Å, b = 4.6335(2) Å, c = 18.4554(8) Å, β = 97.278(2)°, V = 923.85(7) Å^3, Z = 4, T = 225 K, $R_{gt}(F)$ = 0.0385, $wR_{ref}(F^2)$ = 0.0902.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.18 × 0.17 × 0.16 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	4.42 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.6°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11,452, 2095, 0.051
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1618
$N(param)_{refined}$:	119
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3]

Source of material

2,4-Dihydroxybenzaldehyde (276 mg, 2 mmol), 1,2-dibromo propane (374 mg, 2 mmol), of anhydrous potassium bicarbonate (1.38 g) and 15 mL of dry acetone were added to 200 mL of the flask. The mixture was refluxed for 150 h then cool to room temperature. The mixture was filtered and the filtrate was distilled under reduced pressure to obtain yellow residue, which was purified by silica gel chromatography column to obtain a white solid (350 mmg, yield 71.4%, the eluent is a mixture of dichloromethane and petroleum ether in the ratio of 1:2). This white solid is recrystallized in anhydrous ethanol to obtain colorless crystals.

Experimental details

The data were scaled and corrected for absorption using SADABS-2016/2 [2, 3]. The hydrogen atoms were placed at calculated positions as riding atoms with U_{iso}(H) set to 1.2 U_{eq}(C).

Comment

As important chemical intermediates, 4-hydroxybenzalde hyde derivatives can be used to prepare many important active drugs or advanced materials, which have attracted more and more attentions of scientists in recent years [4]. By Knoevenagel reaction, it can be used to synthesize cinnamoyl anthranilates [5], which can reduce fibrosis occurring in the kidney during diabetes. By condensation with thiazolidine-2,4-diones, it can be used to construct novel glitazones [6], which demonstrated excellent antidiabetic activity based on phenoxyalkyl linker. When 4-hydroxybenzaldehyde derivatives reacted with thioalcohol, it can convert to dithioacetal derivatives [7] containing dioxyether moiety, which demonstrated excellent antiviral activities against tobacco mosaic virus activity.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.09391 (3)	−0.01530 (10)	0.28969 (2)	0.05550 (16)
O1	0.18187 (18)	0.0508 (4)	0.46162 (11)	0.0349 (5)
O2	0.3727 (2)	1.0008 (5)	0.69872 (12)	0.0431 (5)
O3	0.46291 (19)	0.6906 (6)	0.59984 (13)	0.0462 (6)
H3	0.4633	0.8126	0.6328	0.069*
C1	0.2138 (3)	−0.2215 (7)	0.35841 (18)	0.0436 (8)
H1A	0.1719	−0.3784	0.3811	0.052*
H1B	0.2773	−0.3071	0.3320	0.052*
C2	0.2736 (3)	−0.0256 (7)	0.41624 (16)	0.0342 (6)
H2A	0.3432	−0.1234	0.4451	0.041*
H2B	0.3049	0.1476	0.3942	0.041*
C3	0.2130 (3)	0.2451 (6)	0.51600 (14)	0.0274 (6)
C4	0.1177 (3)	0.3164 (6)	0.55704 (16)	0.0323 (6)
H4	0.0399	0.2272	0.5474	0.039*
C5	0.1394 (3)	0.5172 (6)	0.61123 (16)	0.0322 (6)
H5	0.0752	0.5666	0.6385	0.039*
C6	0.2549 (3)	0.6513 (6)	0.62719 (15)	0.0284 (6)
C7	0.2748 (3)	0.8730 (6)	0.68230 (16)	0.0336 (6)
H7	0.2079	0.9228	0.7074	0.040*
C8	0.3297 (2)	0.3666 (6)	0.53154 (15)	0.0293 (6)
H8	0.3941	0.3116	0.5050	0.035*
C9	0.3499 (3)	0.5703 (6)	0.58677 (15)	0.0301 (6)

In this paper, we synthesized 4-(2-bromoethoxy)-2-hydroxybenzaldehyde using 2,4-dihydroxybenzaldehyde as starting material. The structure of 4-(2-bromoethoxy)-2-hydroxybenzaldehyde was determined by X-ray single crystal diffraction. As an important variety of 4-hydroxy benzaldehyde derivatives, 4-(2-bromoethoxy)-2-hydroxy benzaldehyde can be used to synthesize nonlinear optical materials [8] after substitution reaction with trimethylamine, condensation reaction with the monoimine tridentate Schiff-base and complexation with the metal cation. In the structure of molecule, the bond length of C1–Br1 is 1.951(4) Å. The bond length of C7–O2 is 1.224(4), which is in normal range [9]. The angle of O2–C7–C6 is 124.6(3)°, which is larger than it of C5–C6–C7 121.0(3)°. The intramolecular, hydrogen bond was observed as following: O3–H3···O2 (d(H14···O2) = 2.611 Å, O3–H···O2 = 147°). But in the structure of a structural analogue (4-hydroxy-3-methoxybenzaldehyde) [10], more hydrogen bonds were observed as following: O11A–H11A···O41Cd(H11A···O41C) = 2.6839 Å; O11A–H11A···O61A d(H11A···O61A) = 2.6758 Å; O11B–H11B···O41D d(H11A···O41D) = 2.7180 Å; O11B–H11B···O61B d(H11A···O61B) = 2.6921 Å; O11C–H11C···O41A d(H11A···O41A) = 2.6914 Å; O11C–H11C···O61C d(H11A···O61C) = 2.6818 Å; O11D–H11D···O41B d(H11A···O41B) = 2.6818 Å; O11D–H11D···O61D d(H11A···O61D) = 2.6932 Å. The π–π stacking forces were observed in both of two crystal sturctures.

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