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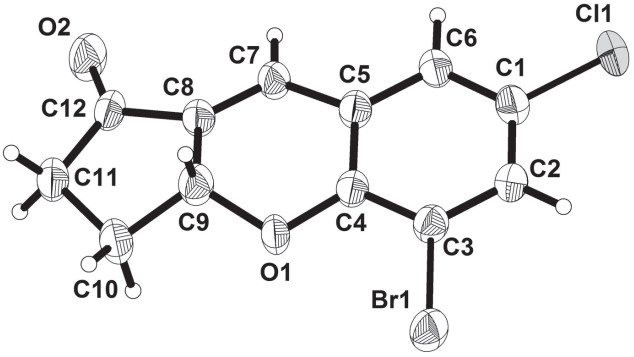
Crystal structure of 5-bromo-7-chloro-3,3*a*-dihydrocyclopenta[*b*]chromen-1(2*H*)-one, $C_{12}H_8BrClO_2$



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Abstract

$C_{12}H_8BrClO_2$, triclinic, $P\bar{1}$ (no. 2), $a = 7.3250(6)$ Å, $b = 8.6187(6)$ Å, $c = 9.9660(6)$ Å, $\alpha = 107.866(2)°$, $\beta = 102.329(2)°$, $\gamma = 105.307(2)°$, $V = 547.06(7)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0487$, $wR_{ref}(F^2) = 0.1166$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized based on the report process [4] as the following steps. Firstly, cyclopent-2-enone (2 mol) and 5-bromo-3-chloro-2-hydroxybenzaldehyde (1 mol) were added to the mixture solvents of THF (1.5 mL) and water (1.5 mL) in a 50 mL round bottom. The mixture was stirred at room temperature. Seventy-two hours later, the reaction was stopped and 1 M HCl (30 mL), was added and stirred about half an hour again. Then we added ehtyl acetate (15 mL) into the system as extractant, separated the ethyl acetate solution, added anhydrous sodium sulfate. The mixture was

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.30 × 0.27 × 0.25 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	3.98 mm^{-1}
Diffractometer, scan mode:	Bruker Photon 100, φ and ω-scans
θ_{max}, completeness:	28.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7605, 2704, 0.024
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2048
$N(param)_{refined}$:	149
Programs:	Bruker programs [1], SHELX [2, 3]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.81338(7)	1.29058(6)	0.46369(5)	0.04682(17)
Cl1	0.8924(2)	0.88216(18)	0.78913(13)	0.0608(4)
O1	0.5469(4)	0.9388(4)	0.2243(3)	0.0392(7)
O2	0.1247(5)	0.3529(4)	−0.0550(4)	0.0542(9)
C1	0.7951(6)	0.8976(6)	0.6203(5)	0.0403(10)
C2	0.8367(6)	1.0591(6)	0.6111(5)	0.0392(9)
H2	0.918191	1.159400	0.694007	0.047*
C3	0.7559(6)	1.0698(5)	0.4773(5)	0.0356(9)
C4	0.6333(6)	0.9209(5)	0.3517(4)	0.0333(8)
C5	0.5920(6)	0.7572(5)	0.3641(4)	0.0351(9)
C6	0.6748(6)	0.7478(6)	0.4985(5)	0.0400(10)
H6	0.649223	0.640036	0.506689	0.048*
C7	0.4449(6)	0.6073(5)	0.2371(4)	0.0372(9)
H7	0.391793	0.501683	0.245968	0.045*
C8	0.3879(6)	0.6240(5)	0.1085(5)	0.0379(9)
C9	0.4826(8)	0.7888(6)	0.0887(5)	0.0457(11)
C10	0.3210(8)	0.7917(6)	−0.0327(5)	0.0522(12)
H10A	0.379139	0.851487	−0.090018	0.063*
H10B	0.237855	0.850128	0.009296	0.063*
C11	0.1987(7)	0.5998(6)	−0.1305(5)	0.0456(11)
H11A	0.059265	0.583703	−0.171254	0.055*
H11B	0.249057	0.559157	−0.212070	0.055*
C12	0.2221(6)	0.5025(5)	−0.0295(4)	0.0388(9)
H9	0.619(8)	0.788(7)	0.051(6)	0.068(17)*

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stored overnight and filtered. The filtrate was concentrated on a rotary evaporator, yielding a yellow solid. Crystals were obtained from petroleum ether and ethyl acetate mixture solvent. The yellow solid was purified by column chromatography on silica (eluted with petroleum ether:ethyl acetate = 3:1, Rf = 0.40). Yield: 39.9%. Anal. Calcd. (%) for $C_{12}H_8BrClO_2$ C, 48.12; H, 2.69; Found (%): C, 49.21; H, 2.74. **^{1}H-NMR** (600 MHz, $CDCl_3$) δH/ppm: 2.06–2.22 (t, 1H, CH_2), 2.34–2.37 (t, 1H, CH_2), 2.62–2.65 (m, 1H, CH_2), 2.79–2.81 (m, 1H, CH_2), 5.34–5.37 (m, 1H, CH), 7.08 (s, 1H, Ar-H), 7.17 (s, 1H, Ar-H), 7.48 (s, 1H, CH = C–).

Experimental details

Hydrogen atoms attached were placed geometrically and refined using a riding model approximation, with C—H = 0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Discussion

There is one title molecule in the asymmetric unit. In the chromene part it's just C9 atom that stretches out from the flat on account of sp^3 hybridization, and other carbons C1—C8 are employing sp^2 hybridization in the chromene ring. Thus the C9 atom adopts a distorted tetrahedron configuration, and the angles change from 104.1(4) to 111.6(4)°. The bond lengths of C4—O1 and C9—O1 are 1.365(5) and 1.433(5) Å, respectively, and C9—C10 is 1.513(6) Å, which is longer than that of C9—C8 1.499(6) Å. Compared with similar structures [4–7], the title compound has two substituent groups on the benzo moiety. In the crystal, intermolecular interactions, which are classified as weak, connect the title molecules.

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