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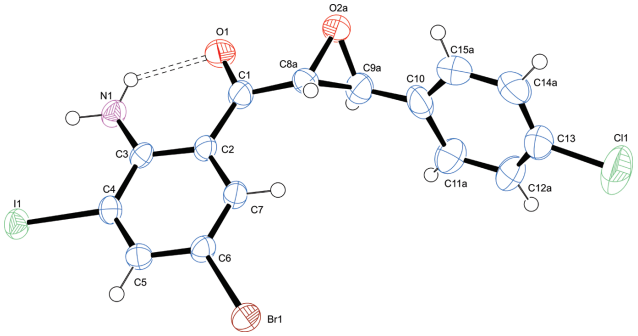
Crystal structure of (2-amino-5-bromo-3-iodophenyl)(3-(4-chlorophenyl)oxiran-2-yl) methanone, $C_{15}H_{10}BrClINO_2$



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Abstract

$C_{15}H_{10}BrClINO_2$, monoclinic, $P2_1/n$ (no. 14), $a = 5.0083(2)$ Å, $b = 9.7548(3)$ Å, $c = 31.9640(10)$ Å, $\beta = 92.576(2)°$, $V = 1560.02(9)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0416$, $wR_{ref}(F_2) = 0.1059$, $T = 173$ K.

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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.

Source of material

A stirred solution of 1-(2-amino-5-bromo-3-iodophenyl)-3-(4-chlorophenyl)prop-2-en-1-one (4.00 g, 4.00 mmol) in a mixture of methanol (100 mL, 1:1 *v*/*v*) and KOH (8 pellets) at 0 °C was reacted in a 100 mL round-bottomed flask. The reaction mixture was treated with H_2O_2 (20 mL) and stirred overnight at room temperature. The mixture

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.62 × 0.48 × 0.30 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	4.79 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Photon, ω
θ_{max}, completeness:	28.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	31032, 3781, 0.058
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3303
$N(param)_{refined}$:	263
Programs:	Bruker [1], WinGX/ORTEP [2], SHELX [3], PLATON [4]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6931(11)	0.6775(5)	0.67719(17)	0.0408(12)
C2	0.4898(9)	0.5747(4)	0.66531(15)	0.0312(9)
C3	0.4385(9)	0.4607(4)	0.69161(14)	0.0283(9)
C4	0.2367(9)	0.3685(5)	0.67779(14)	0.0305(9)
C5	0.0928(9)	0.3865(5)	0.64076(14)	0.0326(9)
H5	−0.040438	0.32449	0.632563	0.039*
C6	0.1472(9)	0.4984(5)	0.61545(14)	0.0314(9)
C7	0.3424(9)	0.5906(5)	0.62729(14)	0.0322(9)
H7	0.377616	0.664382	0.609963	0.039*
C8A[a]	0.7868(15)	0.7760(8)	0.6414(3)	0.037(2)
H8A[a]	0.793134	0.738745	0.613033	0.044*
C9A[a]	0.722(2)	0.9235(10)	0.6460(3)	0.043(2)
H9A[a]	0.615447	0.952881	0.669366	0.052*
O2A[a]	0.9873(14)	0.8721(7)	0.6546(3)	0.060(3)
C8B[b]	0.624(2)	0.8232(11)	0.6627(4)	0.029(3)
H8B[b]	0.435513	0.84887	0.658135	0.035*
C9B[b]	0.821(3)	0.8790(16)	0.6349(5)	0.034(3)
H9B[b]	0.969485	0.822565	0.625842	0.04*
O2B[b]	0.809(2)	0.9229(10)	0.6780(3)	0.047(3)
C10	0.7036(15)	1.0025(7)	0.6060(2)	0.063(2)
C11A[c]	0.445(3)	1.0899(16)	0.6043(5)	0.054(3)
H11A[c]	0.32292	1.086396	0.625353	0.065*
C12A[c]	0.407(3)	1.1752(16)	0.5689(5)	0.054(4)
H12A[c]	0.257531	1.231644	0.56595	0.065*
C11B[c]	0.591(3)	1.1064(14)	0.6093(4)	0.042(3)
H11B[c]	0.537964	1.130583	0.63589	0.05*
C12B[c]	0.530(3)	1.1945(15)	0.5773(5)	0.043(3)
H12B[c]	0.437994	1.274516	0.583214	0.052*
C13	0.5941(13)	1.1729(7)	0.5391(2)	0.0550(15)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C14A[d]	0.833(3)	1.1117(19)	0.5456(5)	0.074(5)
H14A[d]	0.968772	1.127614	0.527237	0.089*
C15A[d]	0.878(3)	1.0277(18)	0.5785(6)	0.068(4)
H15A[d]	1.044275	0.985463	0.581677	0.082*
C14B[d]	0.719(3)	1.0433(14)	0.5298(3)	0.052(3)
H14B[d]	0.747108	1.017962	0.502276	0.062*
C15B[d]	0.797(3)	0.9575(14)	0.5629(4)	0.058(3)
H15B[d]	0.897594	0.878624	0.559318	0.07*
N1	0.5727(9)	0.4440(5)	0.72926(13)	0.0352(9)
O1	0.8370(8)	0.6731(4)	0.70836(12)	0.0467(9)
Cl1	0.5200(5)	1.2815(2)	0.49726(7)	0.0859(6)
Br1	−0.04867(11)	0.51822(6)	0.56198(2)	0.04269(15)
I1	0.14893(7)	0.19560(3)	0.71369(2)	0.03900(12)
H1A	0.546(13)	0.363(7)	0.743(2)	0.055(18)*
H1B	0.713(13)	0.491(7)	0.734(2)	0.048(18)*

[a]Occupancy: 0.626(11), [b]Occupancy: 0.374(11), [c]Occupancy: 0.494(6), [d]Occupancy: 0.506(6).

was then quenched with ice-cold water (200 mL) and the product was extracted into chloroform. The combined organic layers were dried over $MgSO_4$, filtered off and concentrated under reduced pressure on a rotary evaporator to afford the (2-amino-5-bromo-3-iodophenyl)(3-(4-chlorophenyl)oxiran-2-yl)methanone (2.10 g, 54%) as a solid; **mp.** 139–141 °C; ν_{max} **(ATR)** 3458, 3419, 3316, 1654, 1595, 1542, 1515, 1491, 1434, 1188, 1091, 1014, 889, 819, 674, 540, 487, 420 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$) 4.06 (1H, d, $J = 2.0$ Hz, α-H), 4.16 (1H, d, $J = 2.0$ Hz, β-H), 7.02 (2H, br s, NH_2), 7.09 (2H, d, $J = 8.5$ Hz, H-2′,6′), 7.18 (2H, d, $J = 8.5$ Hz, H-3′,5′), 7.86 (1H, d, $J = 2.5$ Hz, H-4), 7.93 (1H, d, $J = 2.0$ Hz, H-6); **^{13}C NMR** (125 MHz, $CDCl_3$) 58.6, 60.1, 87.7, 107.2, 118.0, 125.7, 128.7, 129.1, 133.6, 134.9, 140.1, 146.7, 191.9; **HRMS (ES)**: found. 476.8628 $C_{15}H_{11}BrClINO_2^+$ requires 476.8608.

Experimental details

The intensity of the data was determined on a Bruker Venture D8 Photon CMOS diffractometer with graphite-monochromated MoKα_1 radiation at 173 K using an Oxford Cryostream 600 cooler. Data reduction was carried out using the program SAINT+, version 6.02 [1] and empirical absorption corrections were made using SADABS [1]. The structure was solved in the *WinGX* [2] Suite of programs, using intrinsic phasing through *SHELXT* [3] and refined using *SHELXL-2017* [3]. All C-bound H atoms were placed at idealized positions and refined as riding atoms with isotropic parameters 1.2 times those of their parent atoms. All N-bound H atoms were located in the difference fourier map and their coordinates and isotropic thermal parameters allowed to refine freely. The positional disorder of the epoxide group (labelled C8A/C9A/O1A and C8B/C9B/O1B) was resolved by finding alternative positions in the difference Fourier map and their site occupancies refined to 0.626(11) and 0.374(11). The positional disorder of the phenyl ring (labelled C11A/C12A/C14A/C15A and C11B/C12B/C14B/C15B) was resolved by finding alternative positions in the difference Fourier map and their site occupancies refined to 0.494(6) and 0.506(6). Diagrams and publication material were generated using *ORTEP-3* [2], and *PLATON* [4].

Comment

Aminochalcone epoxides are important substrates for the synthesis of a wide range of natural products and biologically active molecules [5–7]. Epoxychalcones have been found to be biosynthetic intermediates for the rapid construction of complex polycyclic natural products such as flavonoids and their azaflavonoid analogues [8]. The reactivity of the oxirane ring results from its angle strain, which makes the carbon–oxygen bond weaker and more reactive towards nucleophiles than that of ethers [9]. The Weitz–Scheffer reaction, which makes use of hydrogen peroxide under alkaline conditions represents the most efficient method for the oxidation of the α,β-unsaturated ketones into α-epoxyketones [10]. This reaction in the case of 2-aminochalcones is stereospecific and occurs *via syn*-addition with retention of the *trans*-stereochemistry of the parent chalcone. The 2-aminochalcone epoxides exist exclusively in solution and solid state in *trans* geometry with strong intramolecular hydrogen bonding interaction between the amino and carbonyl groups [11]. The previously prepared 1-(2-amino-5-bromo-3-iodophenyl)-3-(4-chlorophenyl)prop-2-en-1-one [12] was subjected to hydrogen peroxide in the presence of aqueous sodium hydroxide in methanol at room temperature for 12 h to obtain the title compound.

Both the ketoaryl and aryl groups are in *trans* orientation relative to each other about the oxirane ring (O_{2a}—C_{8a}—C_{9a}) with a dihedral angle C1—C8a—C9a—C10 = −155.1(7)° (see the figure). In the asymmetric unit, there is hydrogen bonding interaction involving the amino hydrogen atom as a donor and carbonyl oxygen atom as the hydrogen bond acceptor [N(1)—H(1A)···O(1) = 2.46(7) Å and N(1)—H(1B)···O(1) = 2.06 Å] classified using a $R_1^1(6)$ ring graph set descriptor. Both NH_2 hydrogens are involved in the hydrogen bonding. The examination of the short contacts in the crystal structure shows that the molecules are aligned in parallel planes and held together *via* multiple weak C—H···O and C—H···N interactions and further stabilized via π···π stacking.

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