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X-ray Structure Analysis Online

Synthesis and Crystal Structure of 5-Amino-2-benzoxazolone

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5-Amino-2-benzoxazolone crystallizes in an orthorhombic space group, $P2_12_12_1$, with cell dimensions a = 4.4766(12)Å, b = 7.1015(19)Å, c = 20.095(5)Å and V = 6673(3)Å^3, Z = 4. The final R value is 0.0366 for 1487 reflections ($I > 2\sigma(I)$). 2-Benzoxazolone moiety is planar and the title compound exists in a 2-D framework (in crystal lattice), which is produced *via* two different types intermolecular N–H···O hydrogen bonds.

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5-Amino-2-benzoxazolone (Fig. 1) could be useful in a total synthesis of damirazoles,[1] new members of a group of marine alkaloids.[2-4] This compound was easily prepared in good yield by chemical reduction of the corresponding nitro compound. 5-Amino-2-benzoxazolone was prepared by modifications of literature methods.[5,6] 5-Nitro-2-benzoxazolone[7] (0.36 g, 2 mmol) was added as a single portion to an aqueous $TiCl_3$ solution (30%, 7.2 mL, 14 mmol) and the reaction mixture was stirred vigorously for 30 min at room temperature. Then, the reaction mixture was gradually basified with a saturated aqueous $NaHCO_3$ solution, and produced a dark suspension that was filtered. The thus-obtained crude solid was immediately extracted with ethyl acetate several times. The filtered aqueous solution was also extracted with the same solvent (3 × 20 mL). The extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Single crystals of the title compound were obtained from a solution in EtOH after slow evaporation at room temperature.

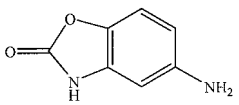

Fig. 1 Chemical structure.

Table 1 Crystal data and structure refinement for the title compound

Formula: $C_7H_6N_2O_2$	
Formula weight = 150.14	
Crystal system: orthorhombic	
Space group: $P2_12_12_1$	Z = 4
a = 4.4766(12)Å	
b = 7.1015(19)Å	
c = 20.095(5)Å	
V = 6673(3)Å^3	
D_x = 1.561 Mg/m^3	
No. of reflections used = 5453	
$2\theta_{max}$ = 56.60 with Mo K_α	
R = 0.0366 [1487 refs. $I > 2\sigma(I)$]	
$(\Delta/\sigma)_{max}$ = 0.000	
$(\Delta\rho)_{max}$ = 0.315 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.201 eÅ^{-3}	
Measurement: Bruker SMART, Bruker SAINT	
Structure determination: SHELXS-97, SHELXL-97, Bruker SHELXTL	
Refinement: full-matrix least-squares on F^2	

CCDC 299817 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data-request/cif

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The crystal and experimental data are given in Table 1. The structure was solved by direct methods. The positions of the hydrogen atoms were obtained from a difference Fourier map. The atomic coordinates for non-hydrogen atoms are listed in Table 2. Selected bond lengths and angles are given in Table 3. In the title compound (Fig. 2), the 2-benzoxazolone moiety is planar (the torsion angles C(6)-C(1)-O(1)-C(7) and C(1)-C(6)-N(1)-C(7) are equal to 0.68(17)° and –1.78(18)°, respectively). Due to a resonance interaction of non-bonding electrons of N(1) with the C=O π system and N(2) with a phenyl

Table 2 Fractional coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) of non-hydrogen atoms

Atom	x	y	z	$U_{(eq)}$
C(1)	9459(3)	3300(2)	8893(1)	15(1)
C(2)	7372(4)	3480(2)	9391(1)	16(1)
C(3)	6151(4)	5267(2)	9481(1)	17(1)
C(4)	7014(3)	6804(2)	9084(1)	16(1)
C(5)	9143(4)	6573(2)	8577(1)	16(1)
C(6)	10315(4)	4794(2)	8493(1)	15(1)
C(7)	12901(4)	2214(2)	8192(1)	18(1)
N(1)	12428(3)	4056(2)	8053(1)	17(1)
N(2)	5846(4)	8599(2)	9207(1)	20(1)
O(1)	11040(3)	1694(2)	8705(1)	18(1)
O(2)	14622(3)	1097(2)	7940(1)	23(1)

$U_{(eq)} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

Table 3 Selected bond lengths (Å) and angles (deg) for title compound

C(1)-C(2)	1.375(2)	C(5)-C(6)	1.378(2)
C(1)-O(1)	1.3942(19)	C(7)-O(2)	1.217(2)
C(4)-N(2)	1.401(2)	C(7)-N(1)	1.355(2)
C(6)-N(1)	1.397(2)	C(7)-O(1)	1.376(2)
C(2)-C(1)-C(6)	122.60(15)	C(5)-C(6)-N(1)	132.73(15)
C(2)-C(1)-O(1)	128.15(14)	O(2)-C(7)-N(1)	129.96(17)
C(6)-C(1)-O(1)	109.25(13)	O(2)-C(7)-O(1)	121.40(16)
C(1)-C(2)-C(3)	116.47(14)	C(7)-N(1)-C(6)	109.70(14)
N(2)-C(4)-C(5)	119.22(15)	C(7)-O(1)-C(1)	106.87(12)

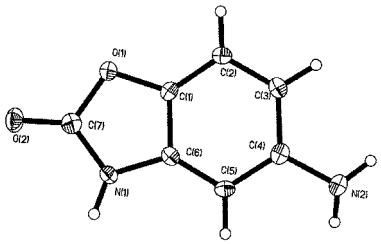

Fig. 2 Molecular structure of title compound, showing the atom-labeling scheme and 50% probability level displacement ellipsoids.

ring, the N(1) atom is planar and the N(2) atom angles are greater than the sp^3 angle (sum of the surrounding angles around N(1) and N(2) are 359.6° and 342.6°, ∠C(7)-N(1)-H(1) = 123.6(15)°, ∠C(7)-N(1)-C(6) = 109.70(14)°, ∠C(6)-N(1)-H(1) = 126.3(15)° and ∠C(4)-N(2)-H(2A) = 115.1(14)°, ∠C(4)-N(2)-H(2B) = 113.5(13)°, ∠H(2B)-N(2)-H(2A) = 114(2)°).

The N(1)-C(7) bond length (1.355 (2)Å) is smaller than a typical C-N single bond length (also, it is shorter than C(6)-N(1) = 1.397(2)Å). The five-membered ring internal angles (C(1)-O(1)-C(7), O(1)-C(7)-N(1), C(7)-N(1)-C(6), N(1)-C(6)-C(1), C(6)-C(1)-O(1)) are in the range of 105.49(14)° - 109.70(14)°. The external angles (C(2)-C(1)-O(1) and C(5)-C(6)-N(1)) of the ring juncture carbon atoms are 128.15(14)° and 132.73(15)°, which show a deviation from the sp^2 angle (although the sum of surrounding angles around C(1) and C(6) are about sp^2 angles). The molecule exists in a 2-D framework, which is produced *via* N(1)-H(1)···O(2) and N(2)-H(2B)···O(2) hydrogen bonds, (Table 4).

Table 4 Hydrogen bond D-H...A for title compound

D-H···A	*d*(D-H)Å	*d*(H···A)Å	*d*(D···A)Å	∠DHA(°)
N(2)-H(2B)...O(2)#1	0.91(2)	2.25(2)	3.151(2)	168(2)
N(1)-H(1)...O(2)#2	0.88(2)	1.92(2)	2.7973(19)	173(2)

Symmetry transformation used to generate equivalent atoms: #1 *x*–1, *y*+1, *z*, #2 –*x*+3, *y*+1/2, –*z*+3/2.

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