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NOTE

Synthesis and Crystal Structure of New Nitrogen Heterocyclic Compound

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An unexpected nitrogen heterocyclic compound has been synthesized originally. Furthermore, the compound was characterized by elemental analysis. The crystal structure of the title compound has been determined by single-crystal X-ray diffraction. It crystallizes in the orthorhombic space group *Pmcn* with a = 12.056(2) Å, b = 4.6016(8) Å, c = 22.185(6) Å, β = 90.00°, Z = 4. There are two fairly strong intramolecular C3-H3···N1 and C5-H5···N2 hydrogen bonds

Keywords: Nitrogen heterocyclic compound, Synthesis, Crystal Structure.

The synthesis of six-membered nitrogen heterocycles by electrocyclic reaction of azatriene systems has been extensively studied[1-5]. A large number of such compounds have been reported with interesting structures because to they play an important role in the field of organic dyes, multifunctional materials, chemical intermediates, *etc*.[6-8]. Recently, a few examples of this kind of reaction were synthesized with catalysis by the free radical 4-methoxy-TEMPO[9] and also carried out by photochemical methods[10,11].

4-Bromobenzaldehyde was purchased from Alfa Aesar and used without further purification. *o*-Aminoacetophenone oxime was synthesized according to an analogous method reported earlier[12]. The other reagents were analytical grade reagents from Tianjin Chemical Reagent Factory. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. X-ray single crystal structure was determined on a Bruker Smart APEX CCD area detector. Melting points were obtained by use of a microscopic melting point apparatus made by Beijing Taike Instrument Limited Company and are uncorrected.

General procedure: To an ethanolic solution (1.5 mL) of 4-bromobenzaldehyde (182.4 mg, 1 mmol) was added an ethanolic solution (1 mL) of *o*-aminoacetophenone oxime (150.2 mg, 1 mmol). After stirring at 55-60 ºC for 12 h, the mixture was filtered, precipitates were collected on a suction filter to afford the unexpected organic compound (278 mg, 88.91 %) as pale yellow powder. m.p. 202-203 ºC. Anal. Calcd for $C_{15}H_{10}N_2Br$ (%): C, 60.42; H, 3.38; N, 9.40. Found (%): C, 60.45; H, 3.41; N, 9.42.

The nitrogen containing heterocyclic compound (2.9 mg, 1 mmol) is dissolved in methylene chloride (2 mL), the colour of the solution is pale yellow, the mixture was filtered and the filtrate was allowed to stand at room temperature for about 2 weeks, the solvent was partially evaporated and obtained pale-yellow block-like single crystals.

X-Ray structure determination: The single crystal of the title nitrogen containing heterocyclic compound, with approximate dimensions of 0.12 × 0.03 × 0.02 mm was placed on a Bruker Smart 1000 diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated MoK$_\alpha$ radition (λ = 0.71073 Å) at 298 (10) K. Data reduction and cell refinement were performed using SAINT[13]. The structure was solved by the direct method (SHELXS-97[14]) and fourier difference techniques and refined by full-matrix least-squares method on F^2 using SHELXL-97[15,16]. Anisotropic thermal parameters were assigned to all atoms. Details of the data collection and refinements of title compound are given in Table-1. CCDC: 1003355

X-ray crystallographic analysis revealed the crystal structure of the title nitrogen heterocyclic compound. And the crystal structure of is only built up by the $C_{15}H_{10}N_2Br$ molecules, in which all bond lengths and angles are in normal ranges. Selected bond distances and angles are listed in Table-2. The molecular structure of the nitrogen heterocyclic compound is shown in Fig. 1. In the crystal structure of the nitrogen heterocyclic compound, there are two pairs of intramolecular C3-H3···N1and C5-H5···N2 hydrogen bonds forming two five-membered rings in the structure of the crystal (Fig. 1). The molecule crystallizes in the monoclinic system, space group *Pmcn*. The packing arrangement of the unit cell of the title nitrogen heterocyclic compound is shown in Fig. 2.

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE TITLE NITROGEN HETEROCYCLIC COMPOUND

Bond	Lengths	Bond	Lengths	Bond	Lengths
Br(1)–C(1)	1.920(9)	N(1)–C(6)	1.355(10)	C(1)–C(2)	1.386(8)
C(6)–C(7)	1.386(10)	N(1)–C(5)	1.309(7)	C(7)–C(6)	1.386(10)
C(8)–C(7)	1.417(13)	C(8)–C(9)	1.260(16)	C(3)–C(2)	1.363(9)
C(4)–C(5)	1.509(12)	C(4)–C(3)	1.393(8)	C(5)–N(1)	1.309(7)
C(9)–C(10)	1.43(2)	C(6)–C(11)	1.431(16)	C(6)–C(12)	1.63(2)
C(11)–C(10)	1.367(19)	-	-	-	-
Bond	**Angles**	**Bond**	**Angles**	**Bond**	**Angles**
C(5)–N(1)–C(6)	116.9(7)	N(1)–C(6)–C(7)	122.9(8)	N(1)–C(6)–C(11)	120.4(9)
N(1)–C(6)–C(12)	112.2(10)	C(7)–C(6)–C(11)	114.8(8)	C(7)–C(6)–C(12)	121.5(10)
C(4)–C(3)–C(2)	112.5(11)	C(8)–C(3)–C(2)	105.5(9)	C(3)–C(4)–C(7)	121.3(13)
C(9)–C(8)–C(7)	120.8(7)	C(9)–C(8)–C(9)	116.8(14)	C(6)–C(7)–C(6)	114.3(9)
C(6)–C(7)–C(8)	122.8(5)	C(3)–C(4)–C(5)	120.7(4)	C(3)–C(4)–C(3)	118.5(9)
N(1)–C(5)–N(1)	126.0(9)	N(1)–C(5)–C(4)	116.9(4)	C(2)–C(1)–Br(1)	119.4(4)
C(2)–C(3)–C(4)	121.2(7)	C(3)–C(2)–C(1)	118.9(7)	C(8)–C(9)–C(10)	119.1(12)
C(2)–C(1)–C(2)	121.3(9)	C(6)–C(11)–H(11)	120.8	C(10)–C(11)–C(6)	118.3(12)
C(11)–C(10)–C(9)	122.3(14)	-	-	-	-

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR THE TITLE NITROGEN HETEROCYCLIC COMPOUND

Empirical formula	$C_{15}H_{10}N_2Br$
Formula weight, (g mol^{-1})	298.16
Temperature, (K)	298.00(10)
Wavelength, (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pmcn*
Cell dimensions (Å,°)	a = 12.056(2), b = 4.6016(8), c = 22.8901(18), α = 90.00, β = 90, γ = 90.00
Volume, (Å^3)	1230.8(5)
Z	4
Density (calculated), (mg/m^3)	1.609
Absorption coefficient, (mm^{-1})	Multi-scan
F(000)	596
Index ranges	-14 ≤ h ≤ 15, -6 ≤ k ≤ 6, -22 ≤ l ≤ 29
Reflections collected	4711/1072 [R_{int} = 0.0683]
Independent reflection	1072
Data/restraints/parameters	1589/0/110
Goodness of fit indicator	1.004
R [I> 2σ(I)]	R_1 = 0.0617, wR_2 = 0.1310
Largest diff. peak and hole, (eÅ^{-3})	0.742 and -0.888

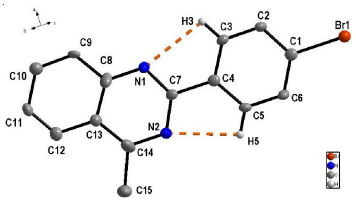

Fig. 1. Crystal structure and intramolecular hydrogen bonds of nitrogen containing heterocyclic compound with atoms numbering (hydrogen atoms, except those forming hydrogen bonds, are omitted for clarity)

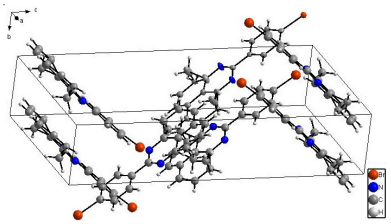

Fig. 2. Packing arrangement of the unit cell of the nitrogen containing heterocyclic compound. (H atoms are omitted for clarity)

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