

# (3S)-3,8-Dibromo-4-phenyl-2,3-dihydro-1H-1,5-benzodiazapin-2-one

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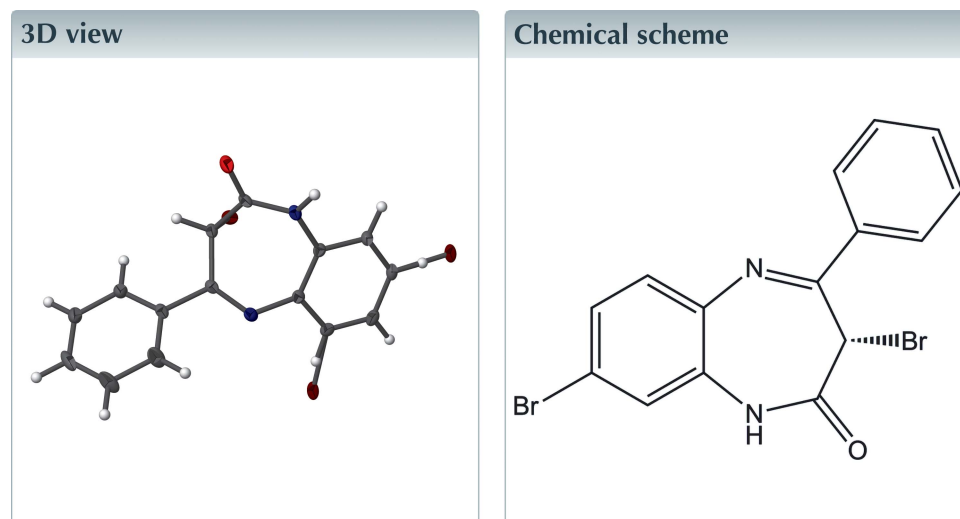
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Structural data: full structural data are available from [iucrdata.iucr.org](http://iucrdata.iucr.org)

In the title compound,  $C_{15}H_{10}Br_2N_2O$ , one Br atom is disordered over two non-chemically equivalent sites, and as a consequence, the crystallized sample contains a mixture of isomers, *viz.* 98.4% of 3,8-dibromo-4-phenyl-2,3-dihydro-1H-1,5-benzodiazapin-2-one and 1.6% of 3,6-dibromo-4-phenyl-2,3-dihydro-1H-1,5-benzodiazapin-2-one. The seven-membered ring adopts a boat conformation. In the crystal, pairwise N—H $\cdots$ O hydrogen bonds form centrosymmetric dimers, which are associated in the crystal through a combination of  $\pi$ - $\pi$  stacking and C—H $\cdots$  $\pi$ (ring) interactions.



## Structure description

Recently there has been considerable interest in the chemistry of 1,5-benzodiazepines. This is undoubtedly due to their broad variety of biological functions such as anti-depressant (Basawaraj *et al.*, 2008), anti-inflammatory (Ha *et al.*, 2010), and antihelmintic activities (Kumar & Joshi, 2008). As a continuation of our studies of new 1,5-benzodiazepin-2-one derivatives (Essaghouani *et al.*, 2016), we report here on the synthesis and structure of the title compound (Fig. 1).

The seven-membered ring adopts a boat conformation with the Br<sub>2</sub> substituent in axial position. A Cremer–Pople puckering analysis of this conformation yielded the parameters  $q_2 = 0.711$  (2),  $q_3 = 0.177$  (2) Å,  $\varphi_2 = 202.1$  (2) and  $\varphi_3 = 309.7$  (7)°.

In the crystal, the molecules form dimers through N2—H2A $\cdots$ O1<sup>i</sup> [symmetry code: (i)  $-x, 1 - y, -z$ ] hydrogen bonds (Table 1 and Fig. 2). These units are further associated by a combination of a  $\pi$ - $\pi$ -stacking interaction between the C10–C15 ring and its counterpart at position  $2 - x, 2 - y, 1 - z$  [centroid-to-centroid distance: 3.592 (2) Å; slip-



20 mmol) in anhydrous  $\text{CHCl}_3$  (40 ml) was refluxed for 6 h. After cooling, the succinimide crystals formed were removed by filtration. The filtrate was evaporated under reduced pressure. The resulting residue was purified by column chromatography (EtOAc/hexane 1/9), to afford the title compound as pale-yellow crystals (yield: 45%).

### Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. In the final stages of the refinement the largest residual peak appeared about 1.7 Å from C5 and in the plane of the C1–C6 ring. Based on trial refinements, this residual was assigned to an alternate location of Br1 with a small occupancy factor. The refinement of this occupancy for the minor isomer converged to 0.0159 (7), while the major isomer contributes to the structure factors with an occupancy of 0.9841 (7).

### Acknowledgements

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## full crystallographic data

*IUCrData* (2017). 2, x170389 [https://doi.org/10.1107/S2414314617003893]

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(3*S*)-3,8-Dibromo-4-phenyl-2,3-dihydro-1*H*-1,5-benzodiazapin-2-one*Crystal data*

$C_{15}H_{10}Br_2N_2O$

$M_r = 394.07$

Triclinic,  $P\bar{1}$

$a = 7.8931$  (8) Å

$b = 9.9295$  (10) Å

$c = 10.2411$  (11) Å

$\alpha = 101.751$  (1)°

$\beta = 105.968$  (2)°

$\gamma = 109.482$  (1)°

$V = 687.77$  (12) Å<sup>3</sup>

$Z = 2$

$F(000) = 384$

$D_x = 1.903$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 8714 reflections

$\theta = 2.2$ – $29.3$ °

$\mu = 5.89$  mm<sup>-1</sup>

$T = 100$  K

Thick plate, light yellow

$0.35 \times 0.31 \times 0.12$  mm

*Data collection*

Bruker SMART APEX CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3333 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2016)

$T_{\min} = 0.39$ ,  $T_{\max} = 0.54$

13311 measured reflections

3674 independent reflections

3263 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 29.3$ °,  $\theta_{\min} = 2.2$ °

$h = -10 \rightarrow 10$

$k = -13 \rightarrow 13$

$l = -14 \rightarrow 14$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.073$

$S = 1.07$

3674 reflections

185 parameters

1 restraint

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: mixed

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 0.8581P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.60$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.70$  e Å<sup>-3</sup>

*Special details*

**Experimental.** The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in  $\omega$ , collected at  $\varphi = 0.00$ , 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in  $\varphi$ , collected at  $\omega = -30.00$  and 210.00°. The scan time was 10 sec/frame.

**Refinement.** H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.98 Å) while those attached to nitrogen were placed in locations derived from a difference map and their coordinates adjusted to give N—H = 0.88 %A. All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. In the final stages of the refinement, a noticeable peak remained about 1.7 Å from C5 while  $U_{\text{iso}}$  for Br1 was distinctly larger than that of Br2. These suggested a small presence of the isomer with Br on C5 instead of C3 and refinement of this model with restraints to make the geometries of the two components comparable led to a ca. 1.4% contribution by the minor isomer.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1A	0.30208 (3)	−0.00789 (2)	0.10256 (3)	0.02206 (8)	0.9841 (7)
Br1B	0.9623 (7)	0.4998 (15)	0.2875 (17)	0.02206 (8)	0.0159 (7)
Br2	0.43259 (3)	0.63603 (3)	0.45110 (2)	0.01890 (7)	
O1	0.1287 (2)	0.67702 (18)	0.1270 (2)	0.0219 (4)	
N1	0.6794 (3)	0.6709 (2)	0.2233 (2)	0.0152 (4)	
N2	0.2434 (3)	0.4979 (2)	0.0929 (2)	0.0148 (4)	
H2A	0.1409	0.4450	0.0133	0.018*	
C1	0.3751 (3)	0.4317 (2)	0.1289 (2)	0.0136 (4)	
C2	0.2943 (3)	0.2749 (2)	0.0982 (2)	0.0146 (4)	
H2	0.1578	0.2193	0.0569	0.018*	
C3	0.4140 (3)	0.2009 (2)	0.1283 (2)	0.0167 (4)	
H3B	0.3576	0.0941	0.1119	0.020*	0.0159 (7)
C4	0.6151 (4)	0.2789 (3)	0.1822 (3)	0.0198 (5)	
H4	0.6967	0.2275	0.2005	0.024*	
C5	0.6922 (3)	0.4333 (3)	0.2082 (3)	0.0186 (4)	
H5A	0.8295	0.4818	0.2423	0.022*	0.9841 (7)
C6	0.5768 (3)	0.5141 (2)	0.1870 (2)	0.0143 (4)	
C7	0.6228 (3)	0.7685 (2)	0.2771 (2)	0.0138 (4)	
C8	0.4336 (3)	0.7311 (2)	0.3006 (2)	0.0147 (4)	
H8	0.4231	0.8285	0.3353	0.018*	
C9	0.2562 (3)	0.6318 (2)	0.1656 (3)	0.0153 (4)	
C10	0.7556 (3)	0.9317 (2)	0.3269 (2)	0.0153 (4)	
C11	0.7572 (4)	1.0337 (3)	0.4444 (3)	0.0255 (5)	
H11	0.6653	1.0001	0.4872	0.031*	
C12	0.8911 (4)	1.1833 (3)	0.4991 (3)	0.0300 (6)	
H12	0.8938	1.2508	0.5809	0.036*	
C13	1.0218 (4)	1.2339 (3)	0.4332 (3)	0.0258 (6)	
H13	1.1106	1.3370	0.4676	0.031*	
C14	1.0214 (4)	1.1344 (3)	0.3188 (3)	0.0293 (6)	
H14	1.1111	1.1688	0.2745	0.035*	
C15	0.8906 (4)	0.9830 (3)	0.2666 (3)	0.0267 (5)	
H15	0.8944	0.9147	0.1888	0.032*	

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1A	0.02331 (13)	0.01058 (11)	0.02899 (14)	0.00794 (9)	0.00466 (10)	0.00528 (9)
Br1B	0.02331 (13)	0.01058 (11)	0.02899 (14)	0.00794 (9)	0.00466 (10)	0.00528 (9)

Br2	0.01833 (12)	0.02158 (12)	0.01888 (12)	0.00794 (9)	0.00865 (9)	0.00892 (9)
O1	0.0149 (8)	0.0127 (7)	0.0306 (10)	0.0059 (6)	-0.0009 (7)	0.0046 (7)
N1	0.0135 (8)	0.0149 (9)	0.0142 (9)	0.0041 (7)	0.0038 (7)	0.0039 (7)
N2	0.0124 (8)	0.0118 (8)	0.0155 (9)	0.0041 (7)	0.0000 (7)	0.0035 (7)
C1	0.0146 (10)	0.0135 (9)	0.0129 (10)	0.0071 (8)	0.0040 (8)	0.0038 (8)
C2	0.0163 (10)	0.0117 (9)	0.0139 (10)	0.0052 (8)	0.0046 (8)	0.0027 (8)
C3	0.0215 (11)	0.0115 (9)	0.0153 (10)	0.0067 (8)	0.0057 (9)	0.0027 (8)
C4	0.0213 (11)	0.0180 (11)	0.0200 (11)	0.0120 (9)	0.0053 (9)	0.0025 (9)
C5	0.0151 (10)	0.0186 (11)	0.0208 (11)	0.0082 (9)	0.0062 (9)	0.0027 (9)
C6	0.0152 (10)	0.0140 (10)	0.0126 (10)	0.0052 (8)	0.0057 (8)	0.0026 (8)
C7	0.0126 (10)	0.0129 (9)	0.0134 (10)	0.0036 (8)	0.0029 (8)	0.0051 (8)
C8	0.0142 (10)	0.0113 (9)	0.0161 (10)	0.0048 (8)	0.0034 (8)	0.0034 (8)
C9	0.0112 (9)	0.0119 (9)	0.0196 (11)	0.0024 (8)	0.0034 (8)	0.0063 (8)
C10	0.0126 (10)	0.0122 (9)	0.0172 (10)	0.0037 (8)	0.0009 (8)	0.0055 (8)
C11	0.0166 (11)	0.0168 (11)	0.0369 (15)	0.0050 (9)	0.0098 (11)	0.0000 (10)
C12	0.0178 (12)	0.0178 (12)	0.0432 (16)	0.0058 (9)	0.0070 (11)	-0.0039 (11)
C13	0.0175 (11)	0.0129 (10)	0.0335 (14)	0.0010 (9)	-0.0037 (10)	0.0079 (10)
C14	0.0275 (14)	0.0253 (13)	0.0238 (13)	-0.0027 (10)	0.0081 (11)	0.0104 (10)
C15	0.0287 (14)	0.0231 (12)	0.0171 (12)	0.0003 (10)	0.0087 (10)	0.0020 (9)

*Geometric parameters (Å, °)*

Br1A—C3	1.891 (2)	C5—C6	1.404 (3)
Br1B—C5	1.879 (4)	C5—H5A	0.9503
Br2—C8	1.964 (2)	C7—C10	1.490 (3)
O1—C9	1.235 (3)	C7—C8	1.513 (3)
N1—C7	1.284 (3)	C8—C9	1.518 (3)
N1—C6	1.406 (3)	C8—H8	1.0000
N2—C9	1.342 (3)	C10—C15	1.381 (3)
N2—C1	1.411 (3)	C10—C11	1.401 (3)
N2—H2A	0.8800	C11—C12	1.387 (3)
C1—C2	1.398 (3)	C11—H11	0.9500
C1—C6	1.403 (3)	C12—C13	1.396 (4)
C2—C3	1.387 (3)	C12—H12	0.9500
C2—H2	0.9500	C13—C14	1.369 (4)
C3—C4	1.395 (3)	C13—H13	0.9500
C3—H3B	0.9600	C14—C15	1.394 (4)
C4—C5	1.383 (3)	C14—H14	0.9500
C4—H4	0.9500	C15—H15	0.9500
C7—N1—C6	123.5 (2)	C10—C7—C8	116.56 (19)
C9—N2—C1	127.68 (19)	C7—C8—C9	113.84 (19)
C9—N2—H2A	116.2	C7—C8—Br2	110.89 (14)
C1—N2—H2A	116.1	C9—C8—Br2	109.57 (14)
C2—C1—C6	120.4 (2)	C7—C8—H8	107.4
C2—C1—N2	116.27 (19)	C9—C8—H8	107.4
C6—C1—N2	123.30 (19)	Br2—C8—H8	107.4
C3—C2—C1	119.8 (2)	O1—C9—N2	122.4 (2)

C3—C2—H2	120.1	O1—C9—C8	118.9 (2)
C1—C2—H2	120.1	N2—C9—C8	118.69 (19)
C2—C3—C4	121.1 (2)	C15—C10—C11	118.5 (2)
C2—C3—Br1A	119.18 (17)	C15—C10—C7	120.8 (2)
C4—C3—Br1A	119.64 (17)	C11—C10—C7	120.4 (2)
C2—C3—H3B	119.4	C12—C11—C10	120.9 (2)
C4—C3—H3B	119.4	C12—C11—H11	119.6
C5—C4—C3	118.1 (2)	C10—C11—H11	119.6
C5—C4—H4	120.9	C11—C12—C13	119.5 (3)
C3—C4—H4	120.9	C11—C12—H12	120.2
C4—C5—C6	122.7 (2)	C13—C12—H12	120.2
C4—C5—Br1B	106.1 (4)	C14—C13—C12	119.8 (2)
C6—C5—Br1B	131.0 (5)	C14—C13—H13	120.1
C4—C5—H5A	115.6	C12—C13—H13	120.1
C6—C5—H5A	121.8	C13—C14—C15	120.7 (3)
C1—C6—C5	117.7 (2)	C13—C14—H14	119.7
C1—C6—N1	127.2 (2)	C15—C14—H14	119.7
C5—C6—N1	115.1 (2)	C10—C15—C14	120.6 (2)
N1—C7—C10	118.3 (2)	C10—C15—H15	119.7
N1—C7—C8	125.11 (19)	C14—C15—H15	119.7
C9—N2—C1—C2	143.1 (2)	N1—C7—C8—C9	-56.2 (3)
C9—N2—C1—C6	-39.4 (3)	C10—C7—C8—C9	126.7 (2)
C6—C1—C2—C3	1.4 (3)	N1—C7—C8—Br2	67.9 (3)
N2—C1—C2—C3	179.0 (2)	C10—C7—C8—Br2	-109.17 (18)
C1—C2—C3—C4	-3.3 (3)	C1—N2—C9—O1	-177.4 (2)
C1—C2—C3—Br1A	174.27 (17)	C1—N2—C9—C8	2.4 (3)
C2—C3—C4—C5	1.6 (4)	C7—C8—C9—O1	-123.5 (2)
Br1A—C3—C4—C5	-176.00 (18)	Br2—C8—C9—O1	111.7 (2)
C3—C4—C5—C6	2.1 (4)	C7—C8—C9—N2	56.7 (3)
C3—C4—C5—Br1B	177.3 (6)	Br2—C8—C9—N2	-68.1 (2)
C2—C1—C6—C5	2.1 (3)	N1—C7—C10—C15	27.1 (3)
N2—C1—C6—C5	-175.4 (2)	C8—C7—C10—C15	-155.6 (2)
C2—C1—C6—N1	179.9 (2)	N1—C7—C10—C11	-147.3 (2)
N2—C1—C6—N1	2.5 (4)	C8—C7—C10—C11	30.0 (3)
C4—C5—C6—C1	-3.9 (4)	C15—C10—C11—C12	0.1 (4)
Br1B—C5—C6—C1	-177.7 (7)	C7—C10—C11—C12	174.6 (2)
C4—C5—C6—N1	178.0 (2)	C10—C11—C12—C13	2.2 (4)
Br1B—C5—C6—N1	4.2 (8)	C11—C12—C13—C14	-2.5 (4)
C7—N1—C6—C1	36.6 (3)	C12—C13—C14—C15	0.5 (4)
C7—N1—C6—C5	-145.5 (2)	C11—C10—C15—C14	-2.0 (4)
C6—N1—C7—C10	172.9 (2)	C7—C10—C15—C14	-176.6 (2)
C6—N1—C7—C8	-4.2 (3)	C13—C14—C15—C10	1.8 (4)

*Hydrogen-bond geometry (Å, °)*

*Cg* is the centroid of the C10–C15 ring.

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N2—H2 <i>A</i> $\cdots$ O1 <sup>i</sup>	0.88	1.99	2.842 (2)	164
C4—H4 $\cdots$ C <i>g</i> 1 <sup>ii</sup>	0.95	0.96	3.824 (3)	151

Symmetry codes: (i)  $-x, -y+1, -z$ ; (ii)  $x, y-1, z$ .