

## 2-(Benzotriazol-1-ylmethylamino)-benzoic acid

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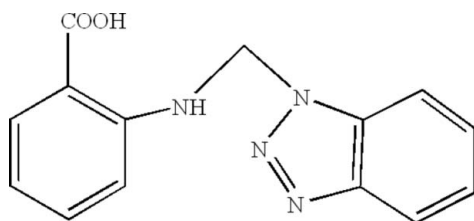
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Key indicators: single-crystal X-ray study;  $T = 291$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.048;  $wR$  factor = 0.118; data-to-parameter ratio = 12.8.

The title compound,  $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_2$ , a new  $N,O,N'$ -tridentate ligand, is V-shaped with the mean plane through the benzotriazole system [planar to within  $0.013$  (2) Å] inclined by  $67.7$  (1)° to the mean plane through the benzene ring. In the molecule there is an intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond involving the amine H atom and the carbonyl O atom. In the crystal structure, symmetry-related molecules are connected by intermolecular  $\text{O}-\text{H}\cdots\text{N}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds and  $\text{C}-\text{H}\cdots\pi$  interactions.

## Related literature

For related literature, see: Trofimenko (1993); Zhang, Dou *et al.* (2007); Zhang *et al.* (2006); Zhang, Zhou *et al.* (2007).



## Experimental

## Crystal data

$\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_2$   
 $M_r = 268.28$

Monoclinic,  $P2_1/c$   
 $a = 10.225$  (6) Å

$b = 15.669$  (8) Å  
 $c = 8.098$  (4) Å  
 $\beta = 97.671$  (7)°  
 $V = 1285.8$  (12) Å<sup>3</sup>  
 $Z = 4$

Mo  $K\alpha$  radiation  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 291$  (2) K  
 $0.19 \times 0.16 \times 0.07$  mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.982$ ,  $T_{\max} = 0.993$   
9692 measured reflections  
2388 independent reflections  
1438 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.053$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.117$   
 $S = 1.02$   
2388 reflections  
186 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.14$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.17$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N4}-\text{H4D}\cdots\text{O1}$	0.86 (2)	1.99 (3)	2.691 (3)	138 (2)
$\text{O2}-\text{H2}\cdots\text{N3}^i$	0.82	1.95	2.746 (3)	165
$\text{C7}-\text{H7A}\cdots\text{O1}^{ii}$	0.97	2.40	3.214 (3)	141
$\text{C12}-\text{H12}\cdots\text{Cg2}^{iii}$	0.93	2.94	3.836 (3)	163

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, -y, -z + 1$ ; (iii)  $-x + 1, -y, -z$ . Cg2 is the centroid of the C1-C6 ring.

Data collection: SMART (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2045).

## References

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**supplementary materials**

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## 2-(Benzotriazol-1-ylmethylamino)benzoic acid

Y. Wang, M.-H. Yin and G.-F. Zhang

### Comment

In last decades, extensive investigations have been undertaken to design and synthesize pyrazole-based tridentate ligands, with the aim of mimicking structures and functions of some metalloenzymes (Trofimenko, 1993). Our interests have been focused on the design and syntheses of flexible *N,O,N* ligands derived from pyrazoles and triazoles since a certain flexibility might afford coordination versatility of the ligands. We have therefore designed and synthesized a number of such ligands as well as their transition-metal complexes (Zhang, Dou *et al.*, 2007; Zhang, Yin *et al.*, 2006; Zhang, Zhou *et al.*, 2007). Here we report on the structure of a new *N,O,N* tridentate ligand, 2-(benzotriazolylmethylamino)benzoic acid.

The molecular structure of the title compound is illustrated in Fig. 1. Details of the hydrogen bonding and C—H $\cdots$  $\pi$  interactions are given in Table 1. The molecule is V-shaped with the best plane through the benzotriazole moiety (planar to within 0.013 (2) Å) inclined by 67.7 (1)° to the best plane through the benzene ring (C8—C13). In the molecule there is an intra-molecular N—H $\cdots$ O hydrogen bond involving the amine (N4) hydrogen, H4D, and the carbonyl O-atom, O1 (Table 1).

In the crystal structure symmetry related molecules form dimers *via* C—H $\cdots$  $\pi$  interactions involving C12—H12 and the benzene ring [(C1—C6 =  $Cg2^{iii}$ )]. Adjacent molecules are linked by O2—H2 $\cdots$ N3<sup>i</sup> hydrogen bonds to form zigzag chains parallel to the *a* axis, and these chains are further linked by C7—H7A $\cdots$ O1<sup>ii</sup> intermolecular hydrogen bonds (Table 1).

### Experimental

The NH hydrogen atom was located from a difference Fourier map and freely refined, N—H = 0.86 (2) Å. The remainder of the H-atoms were included in calculated positions and treated as riding atoms: O—H = 0.82 Å and C—H = 0.93 – 0.97 %A, with  $U_{iso}(H) = 1.5U_{eq}(O)$  and  $1.2U_{eq}(C)$ .

### Figures

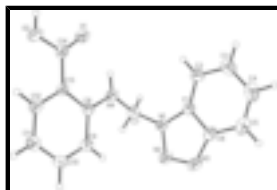


Fig. 1. Molecular structure of the title compound showing the atom numbering scheme and displacement ellipsoids drawn at the 50% probability level.

## 2-(Benzotriazol-1-ylmethylamino)benzoic acid

### Crystal data

C<sub>14</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>

$M_r = 268.28$

$F_{000} = 560$

$D_x = 1.386 \text{ Mg m}^{-3}$

# supplementary materials

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Monoclinic,  $P2_1/c$

$a = 10.225$  (6) Å

$b = 15.669$  (8) Å

$c = 8.098$  (4) Å

$\beta = 97.671$  (7)°

$V = 1285.8$  (12) Å<sup>3</sup>

$Z = 4$

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 1098 reflections

$\theta = 2.4$ – $21.9$ °

$\mu = 0.10$  mm<sup>-1</sup>

$T = 291$  (2) K

Block, colourless

$0.19 \times 0.16 \times 0.07$  mm

## Data collection

Bruker SMART CCD area-detector  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 291$ (2) K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.982$ ,  $T_{\max} = 0.993$

9692 measured reflections

2388 independent reflections

1438 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 25.5$ °

$\theta_{\min} = 2.4$ °

$h = -12 \rightarrow 12$

$k = -18 \rightarrow 18$

$l = -9 \rightarrow 9$

## Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.117$

$S = 1.02$

2388 reflections

186 parameters

Primary atom site location: structure-invariant direct  
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring  
sites

H atoms treated by a mixture of  
independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0885P)^2 + 0.2074P]$$

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

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

$\Delta\rho_{\max} = 0.14$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.17$  e Å<sup>-3</sup>

Extinction correction: none

## Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes)

are estimated using the full covariance matrix. The cell e.s.d.'s are taken

into account individually in the estimation of e.s.d.'s in distances, angles

and torsion angles; correlations between e.s.d.'s in cell parameters are only

used when they are defined by crystal symmetry. An approximate (isotropic)

treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and

goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based

on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of

$F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is

not relevant to the choice of reflections for refinement.  $R$ -factors based

on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -

factors based on ALL data will be even larger.

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.37616 (15)	0.01777 (11)	0.3049 (2)	0.0594 (5)
O2	0.23657 (15)	0.05486 (12)	0.0817 (2)	0.0609 (5)
H2	0.1845	0.0294	0.1327	0.091*
N1	0.85744 (16)	0.01883 (12)	0.3449 (2)	0.0414 (5)
N2	0.95246 (18)	0.05227 (13)	0.2642 (2)	0.0511 (5)
N3	1.02834 (18)	-0.00961 (14)	0.2240 (2)	0.0539 (6)
N4	0.62976 (19)	0.06560 (14)	0.3142 (3)	0.0488 (6)
C1	0.8708 (2)	-0.06775 (14)	0.3566 (3)	0.0393 (5)
C2	0.8006 (2)	-0.13078 (16)	0.4280 (3)	0.0506 (6)
H2A	0.7279	-0.1185	0.4818	0.061*
C3	0.8460 (3)	-0.21219 (17)	0.4134 (3)	0.0635 (8)
H3	0.8022	-0.2567	0.4586	0.076*
C4	0.9558 (3)	-0.23133 (19)	0.3332 (4)	0.0723 (9)
H4	0.9827	-0.2878	0.3270	0.087*
C5	1.0235 (3)	-0.16907 (19)	0.2644 (4)	0.0657 (8)
H5	1.0957	-0.1820	0.2103	0.079*
C6	0.9808 (2)	-0.08513 (16)	0.2776 (3)	0.0462 (6)
C7	0.7583 (2)	0.07434 (15)	0.4056 (3)	0.0479 (6)
H7A	0.7538	0.0612	0.5218	0.057*
H7B	0.7864	0.1333	0.3995	0.057*
C8	0.5883 (2)	0.10492 (13)	0.1642 (3)	0.0377 (5)
C9	0.6766 (2)	0.15121 (14)	0.0805 (3)	0.0488 (6)
H9	0.7650	0.1547	0.1257	0.059*
C10	0.6343 (2)	0.19133 (15)	-0.0668 (3)	0.0578 (7)
H10	0.6946	0.2223	-0.1192	0.069*
C11	0.5051 (3)	0.18711 (16)	-0.1397 (3)	0.0595 (7)
H11	0.4774	0.2150	-0.2396	0.071*
C12	0.4182 (2)	0.14051 (15)	-0.0609 (3)	0.0489 (6)
H12	0.3310	0.1361	-0.1103	0.059*
C13	0.4559 (2)	0.09968 (13)	0.0902 (3)	0.0372 (5)
C14	0.3554 (2)	0.05360 (15)	0.1695 (3)	0.0441 (6)
H4D	0.568 (2)	0.0420 (16)	0.360 (3)	0.068 (9)*

## supplementary materials

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0421 (10)	0.0791 (13)	0.0586 (12)	-0.0032 (9)	0.0122 (9)	0.0203 (10)
O2	0.0344 (9)	0.0840 (14)	0.0641 (12)	-0.0085 (9)	0.0054 (9)	0.0151 (10)
N1	0.0287 (10)	0.0482 (12)	0.0475 (12)	-0.0040 (9)	0.0062 (9)	0.0045 (9)
N2	0.0332 (11)	0.0629 (14)	0.0563 (13)	-0.0067 (10)	0.0030 (10)	0.0090 (11)
N3	0.0342 (11)	0.0726 (15)	0.0552 (13)	-0.0018 (11)	0.0078 (10)	0.0039 (11)
N4	0.0306 (11)	0.0626 (14)	0.0532 (14)	-0.0003 (10)	0.0050 (10)	0.0160 (11)
C1	0.0350 (12)	0.0427 (14)	0.0385 (13)	-0.0007 (11)	-0.0010 (10)	-0.0001 (11)
C2	0.0447 (14)	0.0559 (16)	0.0507 (16)	-0.0061 (13)	0.0050 (12)	0.0067 (13)
C3	0.0670 (19)	0.0527 (18)	0.0670 (19)	-0.0078 (15)	-0.0056 (15)	0.0064 (14)
C4	0.077 (2)	0.0529 (18)	0.082 (2)	0.0130 (16)	-0.0071 (18)	-0.0084 (16)
C5	0.0532 (17)	0.073 (2)	0.070 (2)	0.0111 (15)	0.0053 (14)	-0.0125 (16)
C6	0.0351 (13)	0.0555 (16)	0.0465 (15)	-0.0006 (12)	0.0000 (11)	-0.0029 (12)
C7	0.0418 (14)	0.0496 (15)	0.0520 (15)	0.0025 (12)	0.0055 (11)	0.0017 (12)
C8	0.0368 (12)	0.0336 (12)	0.0436 (14)	0.0024 (10)	0.0094 (11)	0.0011 (10)
C9	0.0360 (13)	0.0501 (15)	0.0611 (17)	-0.0038 (11)	0.0100 (12)	0.0061 (13)
C10	0.0503 (16)	0.0570 (17)	0.0695 (19)	-0.0034 (13)	0.0205 (14)	0.0208 (14)
C11	0.0541 (17)	0.0657 (18)	0.0584 (17)	-0.0023 (14)	0.0061 (13)	0.0207 (14)
C12	0.0406 (13)	0.0565 (16)	0.0488 (15)	-0.0017 (12)	0.0030 (12)	0.0026 (13)
C13	0.0320 (12)	0.0379 (13)	0.0429 (14)	0.0023 (10)	0.0096 (10)	-0.0019 (10)
C14	0.0360 (13)	0.0460 (15)	0.0512 (16)	0.0025 (11)	0.0088 (12)	-0.0011 (12)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

O1—C14	1.225 (3)	C4—C5	1.358 (4)
O2—C14	1.323 (3)	C4—H4	0.9300
O2—H2	0.8200	C5—C6	1.394 (4)
N1—N2	1.347 (2)	C5—H5	0.9300
N1—C1	1.365 (3)	C7—H7A	0.9700
N1—C7	1.470 (3)	C7—H7B	0.9700
N2—N3	1.310 (3)	C8—C9	1.402 (3)
N3—C6	1.371 (3)	C8—C13	1.408 (3)
N4—C8	1.377 (3)	C9—C10	1.367 (3)
N4—C7	1.426 (3)	C9—H9	0.9300
N4—H4D	0.86 (2)	C10—C11	1.375 (3)
C1—C2	1.391 (3)	C10—H10	0.9300
C1—C6	1.393 (3)	C11—C12	1.372 (3)
C2—C3	1.368 (3)	C11—H11	0.9300
C2—H2A	0.9300	C12—C13	1.389 (3)
C3—C4	1.402 (4)	C12—H12	0.9300
C3—H3	0.9300	C13—C14	1.472 (3)
C14—O2—H2	109.5	N4—C7—N1	113.5 (2)
N2—N1—C1	110.39 (18)	N4—C7—H7A	108.9
N2—N1—C7	120.44 (19)	N1—C7—H7A	108.9
C1—N1—C7	129.17 (18)	N4—C7—H7B	108.9

N3—N2—N1	108.78 (18)	N1—C7—H7B	108.9
N2—N3—C6	108.27 (18)	H7A—C7—H7B	107.7
C8—N4—C7	124.7 (2)	N4—C8—C9	121.1 (2)
C8—N4—H4D	114.7 (18)	N4—C8—C13	121.0 (2)
C7—N4—H4D	119.7 (18)	C9—C8—C13	118.0 (2)
N1—C1—C2	133.0 (2)	C10—C9—C8	120.7 (2)
N1—C1—C6	104.0 (2)	C10—C9—H9	119.6
C2—C1—C6	123.0 (2)	C8—C9—H9	119.6
C3—C2—C1	115.2 (2)	C9—C10—C11	121.8 (2)
C3—C2—H2A	122.4	C9—C10—H10	119.1
C1—C2—H2A	122.4	C11—C10—H10	119.1
C2—C3—C4	122.8 (3)	C12—C11—C10	118.1 (2)
C2—C3—H3	118.6	C12—C11—H11	121.0
C4—C3—H3	118.6	C10—C11—H11	121.0
C5—C4—C3	121.3 (3)	C11—C12—C13	122.3 (2)
C5—C4—H4	119.3	C11—C12—H12	118.9
C3—C4—H4	119.3	C13—C12—H12	118.9
C4—C5—C6	117.7 (3)	C12—C13—C8	119.1 (2)
C4—C5—H5	121.2	C12—C13—C14	118.8 (2)
C6—C5—H5	121.2	C8—C13—C14	122.1 (2)
N3—C6—C1	108.6 (2)	O1—C14—O2	121.7 (2)
N3—C6—C5	131.4 (2)	O1—C14—C13	124.6 (2)
C1—C6—C5	120.0 (2)	O2—C14—C13	113.8 (2)
C1—N1—N2—N3	-0.6 (2)	C8—N4—C7—N1	-81.5 (3)
C7—N1—N2—N3	179.61 (18)	N2—N1—C7—N4	109.0 (2)
N1—N2—N3—C6	0.8 (2)	C1—N1—C7—N4	-70.8 (3)
N2—N1—C1—C2	179.3 (2)	C7—N4—C8—C9	6.5 (3)
C7—N1—C1—C2	-0.9 (4)	C7—N4—C8—C13	-173.6 (2)
N2—N1—C1—C6	0.1 (2)	N4—C8—C9—C10	-178.8 (2)
C7—N1—C1—C6	179.9 (2)	C13—C8—C9—C10	1.3 (3)
N1—C1—C2—C3	-179.9 (2)	C8—C9—C10—C11	-0.9 (4)
C6—C1—C2—C3	-0.9 (3)	C9—C10—C11—C12	-0.5 (4)
C1—C2—C3—C4	0.3 (4)	C10—C11—C12—C13	1.5 (4)
C2—C3—C4—C5	-0.2 (4)	C11—C12—C13—C8	-1.1 (3)
C3—C4—C5—C6	0.6 (4)	C11—C12—C13—C14	177.8 (2)
N2—N3—C6—C1	-0.8 (2)	N4—C8—C13—C12	179.8 (2)
N2—N3—C6—C5	179.0 (2)	C9—C8—C13—C12	-0.3 (3)
N1—C1—C6—N3	0.4 (2)	N4—C8—C13—C14	1.0 (3)
C2—C1—C6—N3	-178.9 (2)	C9—C8—C13—C14	-179.1 (2)
N1—C1—C6—C5	-179.4 (2)	C12—C13—C14—O1	-177.4 (2)
C2—C1—C6—C5	1.3 (3)	C8—C13—C14—O1	1.4 (3)
C4—C5—C6—N3	179.1 (2)	C12—C13—C14—O2	1.6 (3)
C4—C5—C6—C1	-1.2 (4)	C8—C13—C14—O2	-179.6 (2)

Hydrogen-bond geometry (Å, °)

<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>
N4—H4D $\cdots$ O1	0.86 (2)	1.99 (3)	2.691 (3)	138 (2)
O2—H2 $\cdots$ N3 <sup>i</sup>	0.82	1.95	2.746 (3)	165

## supplementary materials

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C7—H7A···O1 <sup>ii</sup>	0.97	2.40	3.214 (3)	141
C12—H12···Cg2 <sup>iii</sup>	0.93	2.94	3.836 (3)	163

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



Fig. 1

