

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

A new polymorph of 2-(2H-benzotriazol-2-yl)acetic acid

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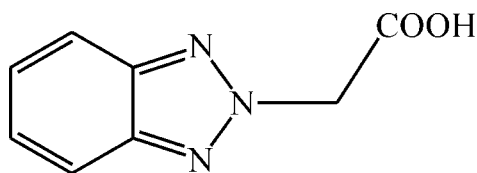
Received 4 July 2012; accepted 24 August 2012

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.036; wR factor = 0.100; data-to-parameter ratio = 12.4.

A new polymorph of 2-(benzotriazol-2-yl)acetic acid, $\text{C}_8\text{H}_7\text{N}_3\text{O}_2$, crystallizes in the space group $C2/c$ ($Z = 8$). The non-planar molecule has a synplanar conformation of the carboxy group. The crystal structure features helices parallel to the b axis sustained by $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonding which are similar to those in the known polymorph [Giordano & Zagari (1978). *J. Chem. Soc. Perkin Trans. 2*, pp. 312–315]. However, in the title structure, columns are formed by $\pi-\pi$ stacking interactions between benzotriazole fragments of centrosymmetrically related adjacent molecules [centroid-centroid distances = 3.593 (10) and 3.381 (10) Å] whereas $\pi-\pi$ stacking interactions are not observed in the other polymorph. In the crystal of the title compound, $\text{C}-\text{H}\cdots\text{O}$ interactions are also observed.

Related literature

For general background to the biological activity of benzotriazole derivatives, see: Hirokawa *et al.* (1998); Yu *et al.* (2003); Kopanska *et al.* (2004). For the previously reported polymorph, see: Giordano & Zagari (1978).



Experimental

Crystal data

$\text{C}_8\text{H}_7\text{N}_3\text{O}_2$
 $M_r = 177.17$
 Monoclinic, $C2/c$
 $a = 11.719$ (9) Å
 $b = 8.308$ (3) Å
 $c = 17.246$ (5) Å
 $\beta = 96.703$ (5)°
 $V = 1667.6$ (15) Å³
 $Z = 8$
 Cu $K\alpha$ radiation
 $\mu = 0.89$ mm⁻¹
 $T = 293$ K
 $0.40 \times 0.32 \times 0.28$ mm

Data collection

Oxford Diffraction Xcalibur, Ruby diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.181$, $T_{\max} = 1.000$
 4907 measured reflections
 1488 independent reflections
 1235 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.100$
 $S = 1.04$
 1488 reflections
 120 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.15$ e Å⁻³
 $\Delta\rho_{\min} = -0.12$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1A}\cdots\text{N3}^{\text{i}}$	0.82	1.91	2.7273 (17)	171
$\text{C2}-\text{H2}\cdots\text{O2}^{\text{ii}}$	0.93	2.54	3.365 (3)	148
$\text{C7}-\text{H7A}\cdots\text{O1}^{\text{iii}}$	0.97	2.49	3.387 (3)	154
$\text{C7}-\text{H7B}\cdots\text{O2}^{\text{iv}}$	0.97	2.39	3.268 (3)	150

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, -y + 1, -z$; (iii) $-x + 2, y, -z + \frac{1}{2}$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

We thank the Academy of Sciences of the Republic of Uzbekistan for supporting this study (grants FA-F3-T045 and FA-F3-T047).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2205).

References

- Giordano, F. & Zagari, A. (1978). *J. Chem. Soc. Perkin Trans. 2*, pp. 312–315.
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supporting information

Acta Cryst. (2012). E68, o2833 [https://doi.org/10.1107/S1600536812036768]

A new polymorph of 2-(2*H*-benzotriazol-2-yl)acetic acid

Guloy Alieva, Jamshid Ashurov, Nasir Mukhamedov and Nusrat Parpiev

S1. Comment

Benzotriazol derivatives exhibit a good degree of analgesic, diuretic, anti-inflammatory, antiviral and antihypertensive activities (Kopanska *et al.*, 2004; Yu *et al.*, 2003; Hirokawa *et al.*, 1998).

In the known polymorphic form (polymorph I) of the title compound reported by Giordano *et al.* (1978) [*J. Chem. Soc., Perkin Trans. 2*, 312–315] the molecules are linked in helices parallel to *b* axis by a strong O—H \cdots N hydrogen bond [D \cdots A = 2.6995 Å; angle D—H \cdots A = 168.08°]. We have now obtained a new polymorph of benzotriazol-2-yl-acetic acid (II), which crystallizes in the space group *C2/c* and its crystal structure is reported here. The asymmetric unit comprises a non-planar independent molecule with a synplanar conformation of the carboxyl group (Fig. 1). Carboxyl group is twisted away from the plane of the 1,2,3-benzotriazol fragment (C1/C2/C3/C4/C5/C6/N1/N2/N3) by 88.41 (15)°. There are helices parallel to *b* axis forming by intermolecular O—H \cdots N hydrogen bonds [D \cdots A = 2.7273 (17) Å; D—H \cdots A = 171°] as in polymorph I (Table 1). Columns form by π - π stacking interactions between benzotriazol fragments of centrosymmetrically related adjacent molecules [centroid-centroid (1.5 - *x*, 0.5 - *y*, -*z*) distance = 3.593 (10) Å, C6 \cdots C6 (1.5 - *x*, 0.5 - *y*, -*z*) distance is 3.381 (10) Å] and [C6 \cdots C2 (1 - *x*, 1 - *y*, -*z*) distance is 3.361 (10) Å]. In the known polymorph I stacking interactions are not observed. The crystal structure of the title compound is further stabilized *via* C—H \cdots O interactions [C2 \cdots O2 = 3.365 (3) Å; angle C2—H2 \cdots O2 = 148°, C7 \cdots O1 = 3.387 (3) Å; angle C7—H7A \cdots O1 = 154°, C7 \cdots O2 = 3.268 (3) Å; angle C7—H7B \cdots O2 = 150°] (Fig. 2).

S2. Experimental

Solid benzotriazol-2-yl-acetic acid was dissolved in dimethylformamide, filtered and left for crystallization by slow evaporation of the solvent at 30°C temperature. Colourless block crystals were obtained after two weeks.

S3. Refinement

H atoms were positioned geometrically, with O—H = 0.82 Å (for OH) and C—H = 0.93 and 0.97 Å for aromatic and methylene H, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

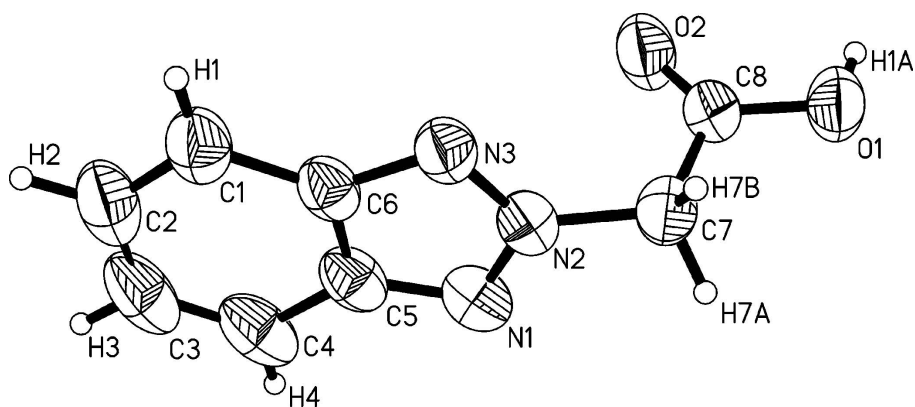


Figure 1

The molecular structure of (II), showing the atom-labelling scheme. Displacements ellipsoids are at the 50% probability level.

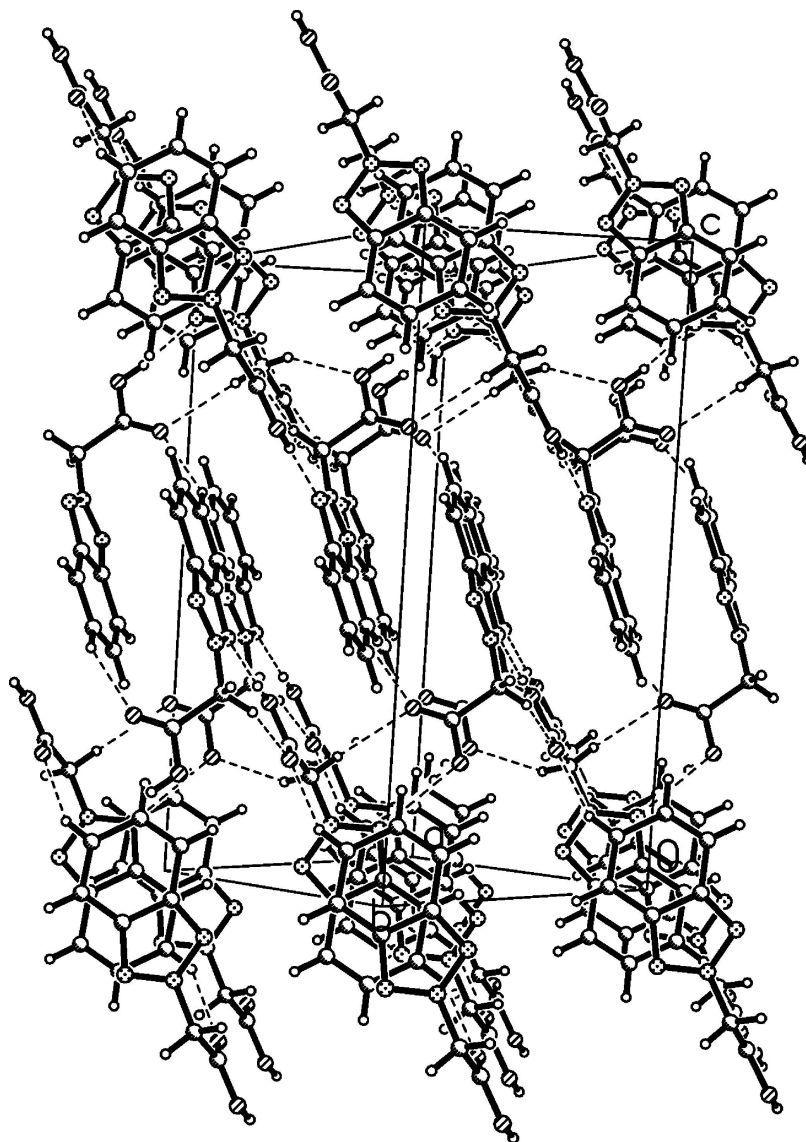


Figure 2

A packing diagram of (II). Hydrogen bonds are shown as dashed lines.

2-(2*H*-benzotriazol-2-yl)acetic acid

Crystal data

$C_8H_7N_3O_2$

$M_r = 177.17$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 11.719 (9) \text{ \AA}$

$b = 8.308 (3) \text{ \AA}$

$c = 17.246 (5) \text{ \AA}$

$\beta = 96.703 (5)^\circ$

$V = 1667.6 (15) \text{ \AA}^3$

$Z = 8$

$F(000) = 736$

$D_x = 1.411 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$

Cell parameters from 408 reflections

$\theta = 5.2\text{--}43.7^\circ$

$\mu = 0.89 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Block, colourless

$0.40 \times 0.32 \times 0.28 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur, Ruby
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.2576 pixels mm⁻¹
 ω scans
Absorption correction: multi-scan
(*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.181$, $T_{\max} = 1.000$

4907 measured reflections
1488 independent reflections
1235 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$
 $\theta_{\max} = 67.1^\circ$, $\theta_{\min} = 5.2^\circ$
 $h = -12 \rightarrow 13$
 $k = -9 \rightarrow 9$
 $l = -20 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.100$
 $S = 1.04$
1488 reflections
120 parameters
0 restraints
Primary atom site location: structure-invariant
direct methods
Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.4124P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0012 (3)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.55191 (14)	0.2934 (2)	-0.01273 (10)	0.0573 (4)
H1	0.5107	0.2146	0.0103	0.069*
C2	0.52406 (16)	0.3401 (2)	-0.08830 (10)	0.0713 (6)
H2	0.4617	0.2915	-0.1175	0.086*
C3	0.58612 (18)	0.4597 (3)	-0.12416 (10)	0.0763 (6)
H3	0.5632	0.4868	-0.1760	0.092*
C4	0.67792 (18)	0.5361 (2)	-0.08543 (9)	0.0682 (5)
H4	0.7186	0.6142	-0.1094	0.082*
C5	0.70856 (14)	0.49131 (18)	-0.00695 (8)	0.0511 (4)
C6	0.64717 (12)	0.37216 (17)	0.02830 (8)	0.0454 (4)
C7	0.85382 (12)	0.48491 (19)	0.18123 (8)	0.0517 (4)
H7A	0.9296	0.5179	0.1701	0.062*
H7B	0.8618	0.3840	0.2096	0.062*
C8	0.80584 (12)	0.61084 (19)	0.23154 (8)	0.0480 (4)

N1	0.79426 (11)	0.54651 (15)	0.04583 (7)	0.0542 (4)
N2	0.78104 (10)	0.46083 (14)	0.10872 (7)	0.0468 (3)
N3	0.69527 (10)	0.35514 (14)	0.10293 (6)	0.0457 (3)
O1	0.87531 (9)	0.63393 (16)	0.29596 (6)	0.0666 (4)
H1A	0.8481	0.7025	0.3227	0.100*
O2	0.71669 (10)	0.67914 (16)	0.21507 (6)	0.0672 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0544 (9)	0.0607 (10)	0.0547 (9)	0.0124 (7)	-0.0024 (7)	-0.0122 (7)
C2	0.0694 (11)	0.0844 (13)	0.0551 (10)	0.0264 (10)	-0.0136 (8)	-0.0231 (9)
C3	0.1008 (15)	0.0870 (13)	0.0384 (9)	0.0391 (12)	-0.0026 (9)	-0.0039 (9)
C4	0.0975 (13)	0.0652 (10)	0.0433 (9)	0.0255 (10)	0.0145 (9)	0.0059 (8)
C5	0.0650 (9)	0.0475 (8)	0.0414 (8)	0.0153 (7)	0.0087 (6)	-0.0012 (6)
C6	0.0507 (8)	0.0468 (8)	0.0383 (7)	0.0133 (6)	0.0031 (6)	-0.0038 (6)
C7	0.0471 (8)	0.0582 (9)	0.0482 (9)	0.0004 (7)	-0.0008 (6)	-0.0039 (7)
C8	0.0475 (8)	0.0574 (9)	0.0386 (7)	-0.0016 (7)	0.0026 (6)	0.0013 (6)
N1	0.0677 (8)	0.0487 (7)	0.0479 (7)	0.0021 (6)	0.0132 (6)	0.0007 (5)
N2	0.0512 (7)	0.0488 (7)	0.0403 (6)	0.0007 (5)	0.0046 (5)	-0.0023 (5)
N3	0.0477 (7)	0.0483 (7)	0.0403 (6)	0.0032 (5)	0.0027 (5)	-0.0008 (5)
O1	0.0524 (6)	0.0924 (9)	0.0518 (7)	0.0143 (6)	-0.0069 (5)	-0.0215 (6)
O2	0.0643 (7)	0.0858 (9)	0.0482 (6)	0.0216 (6)	-0.0072 (5)	-0.0114 (6)

Geometric parameters (Å, °)

C1—C2	1.362 (3)	C6—N3	1.3510 (17)
C1—C6	1.411 (2)	C7—N2	1.4431 (18)
C1—H1	0.9300	C7—C8	1.509 (2)
C2—C3	1.415 (3)	C7—H7A	0.9700
C2—H2	0.9300	C7—H7B	0.9700
C3—C4	1.356 (3)	C8—O2	1.1937 (19)
C3—H3	0.9300	C8—O1	1.3126 (17)
C4—C5	1.409 (2)	N1—N2	1.3214 (17)
C4—H4	0.9300	N2—N3	1.3296 (17)
C5—N1	1.354 (2)	O1—H1A	0.8200
C5—C6	1.403 (2)		
C2—C1—C6	115.77 (18)	C5—C6—C1	121.70 (14)
C2—C1—H1	122.1	N2—C7—C8	111.85 (12)
C6—C1—H1	122.1	N2—C7—H7A	109.2
C1—C2—C3	122.69 (18)	C8—C7—H7A	109.2
C1—C2—H2	118.7	N2—C7—H7B	109.2
C3—C2—H2	118.7	C8—C7—H7B	109.2
C4—C3—C2	122.14 (17)	H7A—C7—H7B	107.9
C4—C3—H3	118.9	O2—C8—O1	124.82 (14)
C2—C3—H3	118.9	O2—C8—C7	124.56 (13)
C3—C4—C5	116.61 (18)	O1—C8—C7	110.62 (13)

C3—C4—H4	121.7	N2—N1—C5	102.73 (13)
C5—C4—H4	121.7	N1—N2—N3	117.02 (11)
N1—C5—C6	108.97 (13)	N1—N2—C7	121.50 (13)
N1—C5—C4	129.93 (17)	N3—N2—C7	121.45 (12)
C6—C5—C4	121.10 (16)	N2—N3—C6	103.30 (11)
N3—C6—C5	107.98 (13)	C8—O1—H1A	109.5
N3—C6—C1	130.32 (14)		

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>
O1—H1A \cdots N3 ⁱ	0.82	1.91	2.7273 (17)	171
C2—H2 \cdots O2 ⁱⁱ	0.93	2.54	3.365 (3)	148
C7—H7A \cdots O1 ⁱⁱⁱ	0.97	2.49	3.387 (3)	154
C7—H7B \cdots O2 ^{iv}	0.97	2.39	3.268 (3)	150

Symmetry codes: (i) $-x+3/2, y+1/2, -z+1/2$; (ii) $-x+1, -y+1, -z$; (iii) $-x+2, y, -z+1/2$; (iv) $-x+3/2, y-1/2, -z+1/2$.