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

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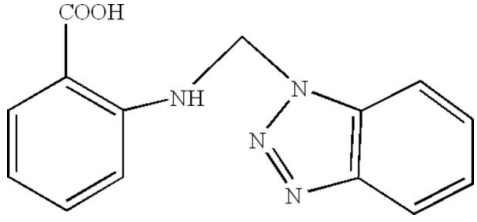
Key indicators: single-crystal X-ray study; $T$ = 291 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.048; $wR$ factor = 0.118; data-to-parameter ratio = 12.8.

The title compound, $C_{14}H_{12}N_4O_2$, 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 N—H···O hydrogen bond involving the amine H atom and the carbonyl O atom. In the crystal structure, symmtry-related molecules are connected by intermolecular O—H···N and C—H···O hydrogen bonds and C—H···$\pi$ 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

$C_{14}H_{12}N_4O_2$
$M_r$ = 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$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.10 mm$^{-1}$
$T$ = 291 (2) K
0.19 × 0.16 × 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 $I > 2\sigma(I)$
$R_{int}$ = 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
$\Delta\rho_{max}$ = 0.14 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N4—H4$D$···O1 | 0.86 (2) | 1.99 (3) | 2.691 (3) | 138 (2) |
| O2—H2···N3$^{i}$ | 0.82 | 1.95 | 2.746 (3) | 165 |
| C7—H7$A$···O1$^{ii}$ | 0.97 | 2.40 | 3.214 (3) | 141 |
| C12—H12···$Cg2^{iii}$ | 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).

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# supporting information

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

**Yao Wang, Mai-Hua Yin and Guo-Fang Zhang**

### S1. Comment

In last decades, extensive investigations have been undertaken to design and synthesize pyrazole-based tridentate ligands, with the aim of mimiking 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 versitality 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···\p 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···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···$\pi$ interactions involving C12—H12 and the benzene ring [(C1—C6 = *Cg*2$^{iii}$]. Adjacent molecules are linked by O2—H2···N3$^{i}$ hydrogen bonds to form zigzag chains parallel to the *a* axis, and these chains are further linked by C7—H7A···O1$^{ii}$ intermolecular hydrogen bonds (Table 1).

### S2. 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) = 1.5$U_{eq}$(O) and 1.2$U_{eq}$(C).

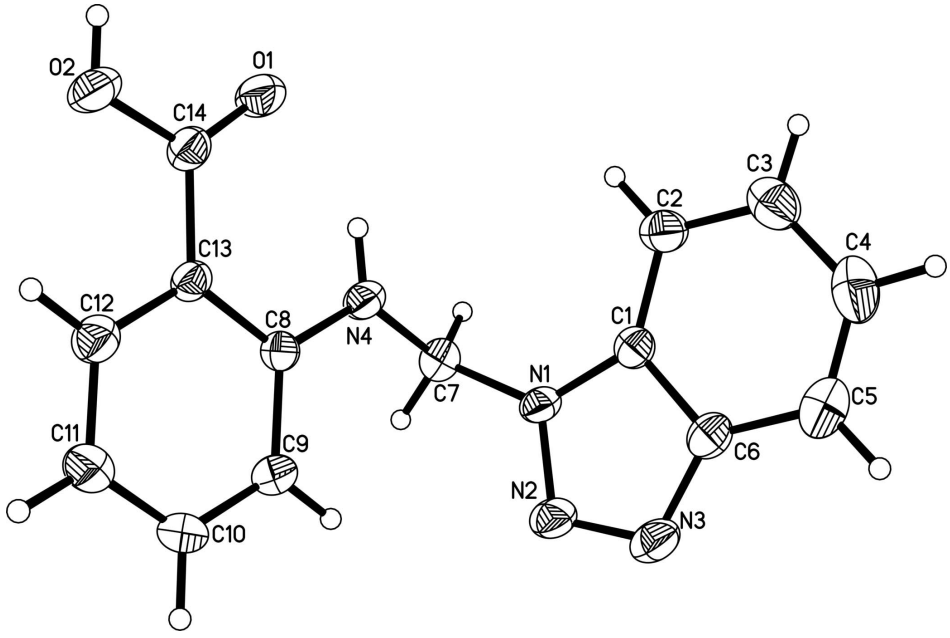


**Figure 1**

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

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

*Crystal data*

$C_{14}H_{12}N_4O_2$
$M_r = 268.28$
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$^3$
$Z = 4$
$F(000) = 560$
$D_x = 1.386$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1098 reflections
$\theta = 2.4–21.9°$
$\mu = 0.10$ mm$^{-1}$
$T = 291$ K
Block, colourless
0.19 × 0.16 × 0.07 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ 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 $I > 2\sigma(I)$
$R_{int} = 0.053$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.4°$
$h = -12\rightarrow12$
$k = -18\rightarrow18$
$l = -9\rightarrow9$

*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
0 restraints
Primary atom site location: structure-invariant direct methods

| | |
|---|---|
| Secondary atom site location: difference Fourier map | $w = 1/[\sigma^2(F_o^2) + (0.0885P)^2 + 0.2074P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| Hydrogen site location: inferred from neighbouring sites | $(\Delta/\sigma)_{max} < 0.001$ |
| H atoms treated by a mixture of independent and constrained refinement | $\Delta\rho_{max} = 0.14$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.17$ e Å$^{-3}$ |

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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 (Å, º)*

| | | | |
|---|---|---|---|
| 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, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N4—H4*D*···O1 | 0.86 (2) | 1.99 (3) | 2.691 (3) | 138 (2) |
| O2—H2···N3$^{i}$ | 0.82 | 1.95 | 2.746 (3) | 165 |
| C7—H7*A*···O1$^{ii}$ | 0.97 | 2.40 | 3.214 (3) | 141 |
| C12—H12···*Cg*2$^{iii}$ | 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*.