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# Ethyl 3-amino-4-[(2-hydroxyethyl)-amino]benzoate

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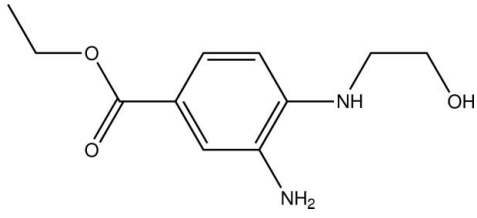
Key indicators: single-crystal X-ray study; $T$ = 296 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.045; $wR$ factor = 0.134; data-to-parameter ratio = 23.1.

In the crystal structure of the title compound, $C_{11}H_{16}N_2O_3$, molecules are linked by one O—H···N and two N—H···O intermolecular hydrogen bonds into a three-dimensional network, which incorporates $R_2^2(14)$ and $R_2^2(16)$ graph-set motifs.

## Related literature

For the biological activity of amino benzoic acid and benzimidazole derivatives, see: Kumar *et al.* (2003); Stefan *et al.* (2002); Pan *et al.* (1999). For related structures, see: Narendra Babu *et al.* (2009); Abdul Rahim *et al.* (2010). For hydrogen-bond motifs, see: Bernstein *et al.* (1995).




## Experimental

### Crystal data

$C_{11}H_{16}N_2O_3$
$M_r$ = 224.26
Monoclinic, $C2/c$
$a$ = 23.2300 (5) Å
$b$ = 14.5914 (4) Å
$c$ = 7.5815 (1) Å
$\beta$ = 108.931 (1)°
$V$ = 2430.81 (9) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 296 K
0.55 × 0.37 × 0.25 mm

### Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min}$ = 0.953, $T_{max}$ = 0.978
26584 measured reflections
3739 independent reflections
2597 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.035

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.134
$S$ = 1.02
3739 reflections
162 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1*O1*···N2$^{i}$ | 0.846 (15) | 2.017 (15) | 2.8628 (14) | 178.4 (14) |
| N2—H1*N2*···O3$^{ii}$ | 0.880 (19) | 2.145 (19) | 3.0083 (16) | 167.0 (13) |
| N2—H2*N2*···O1$^{iii}$ | 0.907 (15) | 2.113 (15) | 2.9800 (14) | 159.7 (13) |

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5088).

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# supporting information

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## Ethyl 3-amino-4-[(2-hydroxyethyl)amino]benzoate

**Natarajan Arumugam, Aisyah Saad Abdul Rahim, Shafida Abd. Hamid, Mohd Mustaqim Rosli and Hoong-Kun Fun**

### S1. Comment

Amino benzoic acid derivatives are important intermediates for the synthesis of various heterocyclic compounds of pharmacological interests (Kumar *et al.*, 2003). The synthesis of novel benzimidazole derivatives such as 2-aminomethyl benzimidazoles (Stefan *et al.*, 2002) and oxobenzimidazoles (Pan *et al.*, 1999) are commonly accessed *via* aminobenzoic acid derivatives. As part of an ongoing study on such compounds, we present the crystal structure of the title compound (I), which was an intermediate in a synthesis.

In the title molecule (Fig. 1), the bond lengths and angles are within normal ranges and are similiar to those in related structures (Narendra Babu *et al.*, 2009; Abdul Rahim *et al.*, 2010). The benzoate group is essentially planar with a maximum deviation of -0.006 (1) for atom C4.

In the crystal structure, molecules are linked by intermolecular N2—H1N2···O3$^{ii}$, N2—H2N2···O1$^{iii}$ and O1—H1O1···N2$^{i}$ hydrogen bonds (see Table 1 for symmetry codes) into a three-dimensional network with $R_2^2(14)$ and $R_2^2(16)$ graph-set motifs (Bernstein *et al.*, 1995).

### S2. Experimental

Ethyl 4-(2-hydroxyethylamino)-3-nitro-benzoate (0.5 g, 1.96 mmol), ammonium formate (0.4 g, 6.8 mmol) and palladium on carbon (250 mg) were mixed in ethanol. The reaction mixture was irradiated under microwave conditions at 373K for 2 minutes. After completion, the reaction mixture was filtered through celite and the filtrate was concentrated under reduced pressure to yield the crude product. The product was recrystallised from EtOAc to afford the title compound as colourless crystals.

### S3. Refinement

N-bound and O-bound H atoms were located from a difference Fourier map and refined isotropically. The remaining H atoms were positioned geometrically [C-H = 0.93, 0.96 or 0.97 Å] and were refined using a riding model, with $U_{iso}$(H) = x$U_{eq}$(C), where x = 1.5 for methyl and 1.2 for all other atoms. A rotating model was used for the methyl group.

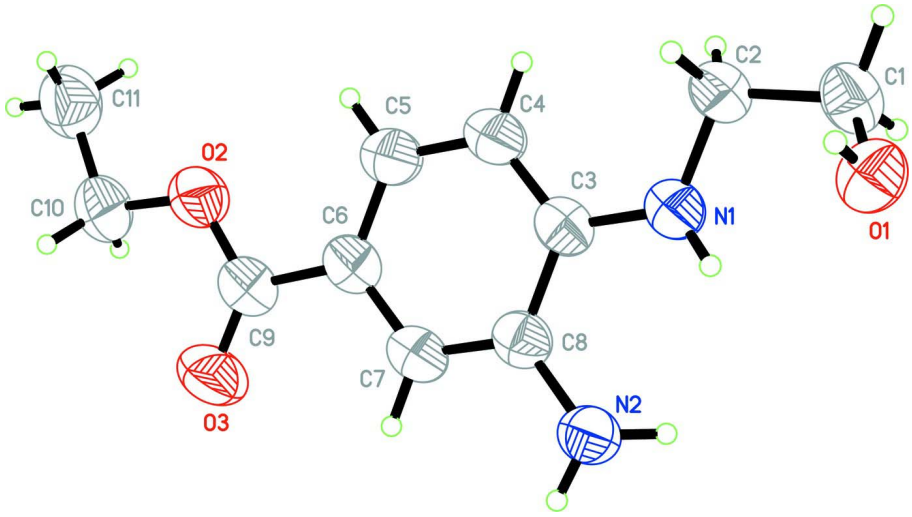


**Figure 1**

The molecular structure, showing 50% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen atoms are shown as spheres of arbitrary radius.

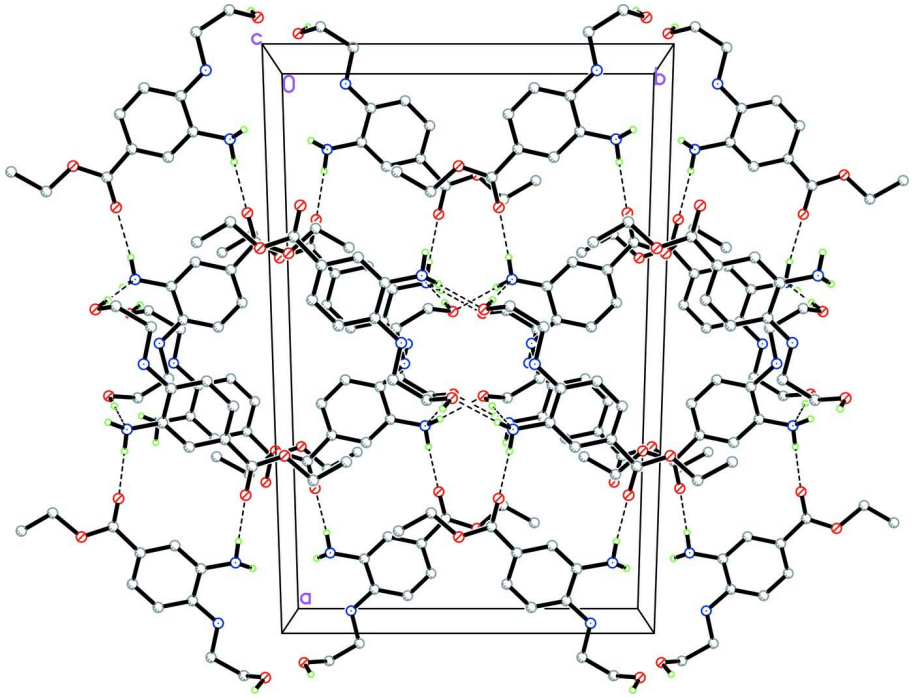


**Figure 2**

The crystal packing of (I) viewed along the c axis. Dashed lines indicate hydrogen bonds. H atoms not involved in the hydrogen bond interactions have been omitted for clarity.

## Ethyl 3-amino-4-[(2-hydroxyethyl)amino]benzoate

*Crystal data*

$C_{11}H_{16}N_2O_3$
$M_r = 224.26$

Monoclinic, $C2/c$
Hall symbol: -C 2yc

$a$ = 23.2300 (5) Å
$b$ = 14.5914 (4) Å
$c$ = 7.5815 (1) Å
$\beta$ = 108.931 (1)°
$V$ = 2430.81 (9) Å$^3$
$Z$ = 8
$F$(000) = 960
$D_x$ = 1.226 Mg m$^{-3}$

Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 8941 reflections
$\theta$ = 2.8–30.6°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 296 K
Block, colourless
0.55 × 0.37 × 0.25 mm

*Data collection*

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min}$ = 0.953, $T_{max}$ = 0.978

26584 measured reflections
3739 independent reflections
2597 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.035
$\theta_{max}$ = 30.6°, $\theta_{min}$ = 1.7°
$h$ = −32→33
$k$ = −20→20
$l$ = −10→10

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.134
$S$ = 1.02
3739 reflections
162 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 atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0626P)^2 + 0.4393P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.21 e Å$^{-3}$

*Special details*

**Geometry**. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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$^2$ > 2sigma(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 (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | −0.07544 (4) | 0.04108 (6) | −0.13906 (13) | 0.0595 (2) |
| O2 | 0.17663 (4) | 0.52426 (6) | 0.03582 (14) | 0.0667 (3) |
| O3 | 0.24606 (4) | 0.41940 (7) | 0.03351 (18) | 0.0826 (3) |
| N1 | 0.01804 (4) | 0.17082 (8) | 0.01775 (14) | 0.0544 (2) |
| N2 | 0.13085 (5) | 0.11676 (7) | 0.00330 (14) | 0.0540 (2) |
| C1 | −0.07977 (6) | 0.10608 (9) | −0.00450 (17) | 0.0581 (3) |
| H1A | −0.0643 | 0.0789 | 0.1186 | 0.070* |
| H1B | −0.1223 | 0.1212 | −0.0277 | 0.070* |

| | | | | |
|---|---|---|---|---|
| C2 | −0.04490 (5) | 0.19272 (8) | −0.00811 (16) | 0.0521 (3) |
| H2A | −0.0627 | 0.2237 | −0.1266 | 0.063* |
| H2B | −0.0472 | 0.2336 | 0.0903 | 0.063* |
| C3 | 0.05994 (5) | 0.23731 (8) | 0.01945 (15) | 0.0490 (3) |
| C4 | 0.04734 (5) | 0.33047 (8) | 0.02461 (19) | 0.0600 (3) |
| H4A | 0.0091 | 0.3487 | 0.0258 | 0.072* |
| C5 | 0.09038 (6) | 0.39616 (9) | 0.0280 (2) | 0.0623 (3) |
| H5A | 0.0809 | 0.4579 | 0.0308 | 0.075* |
| C6 | 0.14783 (5) | 0.37052 (8) | 0.02717 (16) | 0.0539 (3) |
| C7 | 0.16117 (5) | 0.27727 (8) | 0.02449 (15) | 0.0518 (3) |
| H7A | 0.1997 | 0.2597 | 0.0254 | 0.062* |
| C8 | 0.11884 (5) | 0.21078 (8) | 0.02050 (14) | 0.0479 (2) |
| C9 | 0.19533 (5) | 0.43832 (9) | 0.03180 (17) | 0.0575 (3) |
| C10 | 0.21965 (6) | 0.59737 (9) | 0.0476 (2) | 0.0668 (3) |
| H10A | 0.2336 | 0.5963 | −0.0598 | 0.080* |
| H10B | 0.2546 | 0.5910 | 0.1595 | 0.080* |
| C11 | 0.18689 (8) | 0.68429 (11) | 0.0526 (3) | 0.0838 (5) |
| H11A | 0.2149 | 0.7347 | 0.0733 | 0.126* |
| H11B | 0.1697 | 0.6817 | 0.1519 | 0.126* |
| H11C | 0.1550 | 0.6926 | −0.0640 | 0.126* |
| H1O1 | −0.0924 (7) | 0.0638 (11) | −0.246 (2) | 0.075 (4)* |
| H1N1 | 0.0238 (6) | 0.1165 (11) | −0.0138 (19) | 0.065 (4)* |
| H1N2 | 0.1691 (8) | 0.1076 (10) | 0.012 (2) | 0.072 (4)* |
| H2N2 | 0.1176 (7) | 0.0761 (10) | 0.072 (2) | 0.071 (4)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0687 (5) | 0.0560 (5) | 0.0529 (5) | 0.0008 (4) | 0.0184 (4) | 0.0009 (4) |
| O2 | 0.0536 (5) | 0.0594 (5) | 0.0905 (7) | −0.0071 (4) | 0.0280 (4) | −0.0010 (4) |
| O3 | 0.0551 (5) | 0.0787 (7) | 0.1247 (9) | −0.0041 (4) | 0.0441 (5) | −0.0072 (6) |
| N1 | 0.0481 (5) | 0.0538 (6) | 0.0645 (6) | −0.0011 (4) | 0.0226 (4) | −0.0009 (4) |
| N2 | 0.0508 (5) | 0.0569 (6) | 0.0567 (6) | 0.0036 (4) | 0.0210 (4) | −0.0002 (4) |
| C1 | 0.0572 (6) | 0.0655 (7) | 0.0577 (7) | −0.0079 (5) | 0.0270 (5) | −0.0043 (5) |
| C2 | 0.0481 (6) | 0.0587 (6) | 0.0534 (6) | −0.0015 (5) | 0.0218 (5) | −0.0029 (5) |
| C3 | 0.0452 (5) | 0.0574 (6) | 0.0461 (5) | −0.0014 (4) | 0.0172 (4) | −0.0015 (4) |
| C4 | 0.0462 (6) | 0.0590 (7) | 0.0794 (8) | 0.0021 (5) | 0.0266 (6) | −0.0004 (6) |
| C5 | 0.0533 (6) | 0.0541 (7) | 0.0839 (8) | 0.0020 (5) | 0.0285 (6) | −0.0005 (6) |
| C6 | 0.0475 (6) | 0.0594 (7) | 0.0575 (6) | −0.0028 (5) | 0.0207 (5) | −0.0018 (5) |
| C7 | 0.0436 (5) | 0.0638 (7) | 0.0501 (6) | 0.0018 (5) | 0.0180 (4) | −0.0015 (5) |
| C8 | 0.0474 (5) | 0.0561 (6) | 0.0411 (5) | 0.0021 (4) | 0.0154 (4) | −0.0011 (4) |
| C9 | 0.0510 (6) | 0.0643 (7) | 0.0600 (7) | −0.0028 (5) | 0.0219 (5) | −0.0024 (5) |
| C10 | 0.0603 (7) | 0.0693 (8) | 0.0737 (8) | −0.0151 (6) | 0.0257 (6) | −0.0026 (6) |
| C11 | 0.0976 (11) | 0.0696 (9) | 0.0974 (12) | −0.0124 (8) | 0.0499 (9) | −0.0071 (8) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.4203 (15) | C3—C4 | 1.3938 (17) |
| O1—H1O1 | 0.844 (17) | C3—C8 | 1.4194 (15) |
| O2—C9 | 1.3306 (16) | C4—C5 | 1.3792 (17) |
| O2—C10 | 1.4447 (15) | C4—H4A | 0.9300 |
| O3—C9 | 1.2065 (15) | C5—C6 | 1.3880 (16) |
| N1—C3 | 1.3714 (14) | C5—H5A | 0.9300 |
| N1—C2 | 1.4465 (14) | C6—C7 | 1.3972 (18) |
| N1—H1N1 | 0.851 (15) | C6—C9 | 1.4738 (17) |
| N2—C8 | 1.4144 (15) | C7—C8 | 1.3747 (16) |
| N2—H1N2 | 0.880 (17) | C7—H7A | 0.9300 |
| N2—H2N2 | 0.907 (16) | C10—C11 | 1.486 (2) |
| C1—C2 | 1.5064 (17) | C10—H10A | 0.9700 |
| C1—H1A | 0.9700 | C10—H10B | 0.9700 |
| C1—H1B | 0.9700 | C11—H11A | 0.9600 |
| C2—H2A | 0.9700 | C11—H11B | 0.9600 |
| C2—H2B | 0.9700 | C11—H11C | 0.9600 |
| | | | |
| C1—O1—H1O1 | 107.8 (11) | C4—C5—H5A | 119.8 |
| C9—O2—C10 | 118.22 (10) | C6—C5—H5A | 119.8 |
| C3—N1—C2 | 121.87 (10) | C5—C6—C7 | 118.72 (11) |
| C3—N1—H1N1 | 119.1 (10) | C5—C6—C9 | 122.18 (11) |
| C2—N1—H1N1 | 114.3 (10) | C7—C6—C9 | 119.10 (10) |
| C8—N2—H1N2 | 111.4 (10) | C8—C7—C6 | 121.82 (10) |
| C8—N2—H2N2 | 117.9 (9) | C8—C7—H7A | 119.1 |
| H1N2—N2—H2N2 | 112.2 (13) | C6—C7—H7A | 119.1 |
| O1—C1—C2 | 112.55 (9) | C7—C8—N2 | 121.69 (10) |
| O1—C1—H1A | 109.1 | C7—C8—C3 | 119.27 (10) |
| C2—C1—H1A | 109.1 | N2—C8—C3 | 118.86 (10) |
| O1—C1—H1B | 109.1 | O3—C9—O2 | 122.72 (12) |
| C2—C1—H1B | 109.1 | O3—C9—C6 | 124.60 (12) |
| H1A—C1—H1B | 107.8 | O2—C9—C6 | 112.68 (10) |
| N1—C2—C1 | 109.76 (10) | O2—C10—C11 | 106.38 (11) |
| N1—C2—H2A | 109.7 | O2—C10—H10A | 110.5 |
| C1—C2—H2A | 109.7 | C11—C10—H10A | 110.5 |
| N1—C2—H2B | 109.7 | O2—C10—H10B | 110.5 |
| C1—C2—H2B | 109.7 | C11—C10—H10B | 110.5 |
| H2A—C2—H2B | 108.2 | H10A—C10—H10B | 108.6 |
| N1—C3—C4 | 122.37 (10) | C10—C11—H11A | 109.5 |
| N1—C3—C8 | 119.14 (10) | C10—C11—H11B | 109.5 |
| C4—C3—C8 | 118.47 (10) | H11A—C11—H11B | 109.5 |
| C5—C4—C3 | 121.38 (11) | C10—C11—H11C | 109.5 |
| C5—C4—H4A | 119.3 | H11A—C11—H11C | 109.5 |
| C3—C4—H4A | 119.3 | H11B—C11—H11C | 109.5 |
| C4—C5—C6 | 120.33 (11) | | |
| | | | |
| C3—N1—C2—C1 | 179.71 (10) | C6—C7—C8—C3 | −0.13 (16) |

| | | | |
|---|---|---|---|
| O1—C1—C2—N1 | −56.17 (13) | N1—C3—C8—C7 | −179.22 (10) |
| C2—N1—C3—C4 | 9.84 (17) | C4—C3—C8—C7 | −0.70 (16) |
| C2—N1—C3—C8 | −171.70 (10) | N1—C3—C8—N2 | 5.47 (15) |
| N1—C3—C4—C5 | 179.39 (12) | C4—C3—C8—N2 | −176.01 (10) |
| C8—C3—C4—C5 | 0.93 (18) | C10—O2—C9—O3 | −1.65 (19) |
| C3—C4—C5—C6 | −0.3 (2) | C10—O2—C9—C6 | 177.74 (10) |
| C4—C5—C6—C7 | −0.54 (19) | C5—C6—C9—O3 | 179.09 (13) |
| C4—C5—C6—C9 | −179.63 (12) | C7—C6—C9—O3 | 0.0 (2) |
| C5—C6—C7—C8 | 0.76 (17) | C5—C6—C9—O2 | −0.29 (17) |
| C9—C6—C7—C8 | 179.87 (10) | C7—C6—C9—O2 | −179.38 (10) |
| C6—C7—C8—N2 | 175.04 (10) | C9—O2—C10—C11 | −179.15 (12) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*O*1···N2$^{i}$ | 0.846 (15) | 2.017 (15) | 2.8628 (14) | 178.4 (14) |
| N2—H1*N*2···O3$^{ii}$ | 0.880 (19) | 2.145 (19) | 3.0083 (16) | 167.0 (13) |
| N2—H2*N*2···O1$^{iii}$ | 0.907 (15) | 2.113 (15) | 2.9800 (14) | 159.7 (13) |

Symmetry codes: (i) −*x*, *y*, −*z*−1/2; (ii) −*x*+1/2, −*y*+1/2, −*z*; (iii) −*x*, −*y*, −*z*.