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## Structure Reports

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## Ethyl 2-[(Z)-2-benzylhydrazin-1-ylidene]-2-bromoacetate

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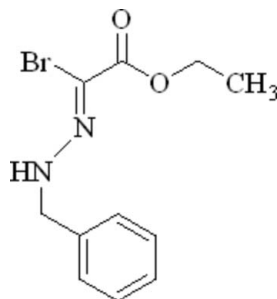
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Key indicators: single-crystal X-ray study;  $T = 294$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.038;  $wR$  factor = 0.111; data-to-parameter ratio = 15.0.

In the title compound,  $\text{C}_{11}\text{H}_{13}\text{BrN}_2\text{O}_2$ , the dihedral angle between the phenyl ring and the almost planar (r.m.s. deviation = 0.011 Å)  $\text{C}-\text{C}(\text{Br})=\text{N}-\text{N}(\text{H})-$  fragment is  $74.94(16)^\circ$ . In the crystal, molecules are linked by  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds, which generate  $C(6)$  chains propagating in [010]. Weak aromatic  $\pi-\pi$  stacking [centroid-centroid separation =  $3.784(3)$  Å] may also help to consolidate the packing.

## Related literature

For the use of the title compound in the preparation of heterocyclic compounds *via* the dipolar cycloaddition of thiadiazole, see Feddoui *et al.* (2004); Abouricha *et al.* (2005); Hafez *et al.* (2008). For the synthesis of the title compound, see Bach *et al.* (1994).



## Experimental

## Crystal data

$\text{C}_{11}\text{H}_{13}\text{BrN}_2\text{O}_2$   
 $M_r = 285.14$   
 Monoclinic,  $P2_1/c$   
 $a = 9.046(1)$  Å  
 $b = 11.235(1)$  Å  
 $c = 12.326(2)$  Å  
 $\beta = 92.935(4)^\circ$   
 $V = 1251.1(3)$  Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 3.27$  mm<sup>-1</sup>  
 $T = 294$  K  
 $0.25 \times 0.14 \times 0.07$  mm

## Data collection

Siemens APEX CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Siemens, 1996)  
 $T_{\min} = 0.495$ ,  $T_{\max} = 0.803$   
 4952 measured reflections  
 2188 independent reflections  
 1475 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.019$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.111$   
 $S = 1.02$   
 2188 reflections  
 146 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.26$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.61$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$                   | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N1}-\text{H1}\cdots\text{O1}^i$ | 0.86         | 2.24               | 2.965 (4)   | 141                  |

Symmetry code: (i)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ .

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); 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: HB5585).

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## supporting information

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**Ethyl 2-[(Z)-2-benzylhydrazin-1-ylidene]-2-bromoacetate****Qian-Jiao Yang, Dan Liu, Jian Zuo, Guo-Dong Hu and Lin-Xiang Zhao****S1. Comment**

(Benzylhydrazono)acetate is a key intermediate in the preparation for pyrazoline compounds (Bach *et al.*, 1994), which are selective for the NMDA receptors and show weak antagonists. In addition, it plays an important role in the synthesis of thiadiazole nucleus (Feddouli *et al.*, 2004; Abouricha *et al.*, 2005), which have been exhibited potential anti-inflammatory and analgesic activities (Hafez *et al.*, 2008). Herein, the structure of ethyl 2-bromo-(Z)-2-(2-benzylhydrazono)acetate has been determined.

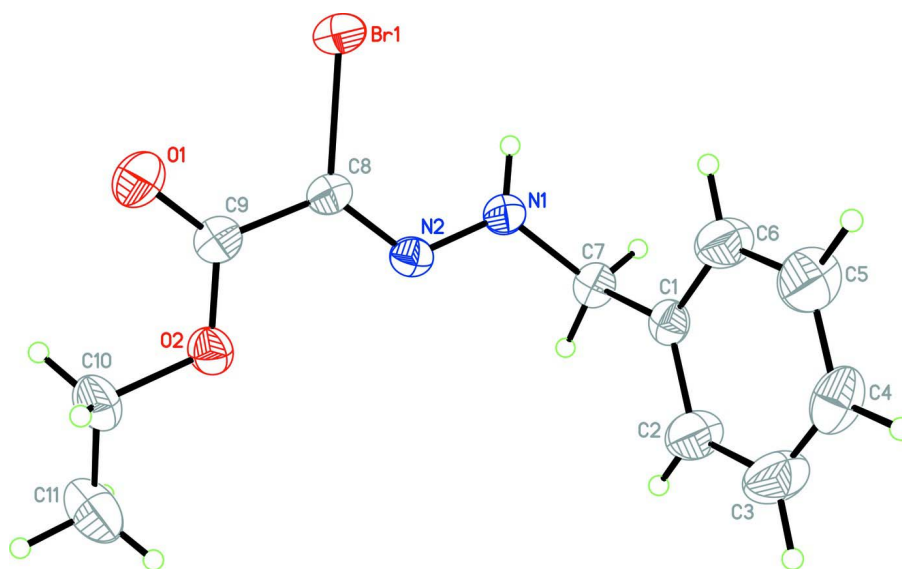
The crystal structure of the title compound is given in Fig. 1. In the crystal, the adjacent molecules are stabilized by N—H···O hydrogen bonding, with the distance of 2.965 (4) Å (Table 1). Molecules are linked into chain along the *b* axis by the above hydrogen bond (Fig. 2).

**S2. Experimental**

To a stirred solution of ethyl 2,2-diethoxyacetate (1 ml, 5.6 mmol) and acetyl chloride (0.8 ml, 11.2 mmol) was added iodine (3 mg, 0.01 mmol). After the mixture was stirred for overnight, excess acetyl chloride was removed *in vacuo*, the residue in 1,4-dioxane (25 ml) was treated with benzylhydrazine dihydrochloride (1.09 g, 5.6 mmol) in water (10 ml), then the mixture was adjusted to pH 4. After 1 h the mixture was neutralized to pH 8 with saturated NaOH and evaporated *in vacuo*. The residue was added water and extracted with CH<sub>2</sub>Cl<sub>2</sub>, the organic layer was dried over MgSO<sub>4</sub>, filtered and concentrated. The crude compound was dissolved in AcOEt (8 ml), which was reacted with NBS (1.1 g, 6.2 mmol) for 2 h. After evaporation of the solvent, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered, the filtrate was concentrated and purified by column chromatography (eluent: PE/AcOEt = 28/1) to give the title compound (0.67 g, 2.35 mmol) as a white solid. Colorless blocks of (I) were grown in PE/AcOEt (14/0.5, V/V) solution by slow evaporation at room temperature.

**S3. Refinement**

All H-atoms were positioned geometrically and refined using a riding model, with C—H = 0.96 Å (methyl), 0.97 Å (methenyl), 0.93 Å (aromatic), and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .



**Figure 1**

The structure of (I) showing 30% probability displacement ellipsoids.

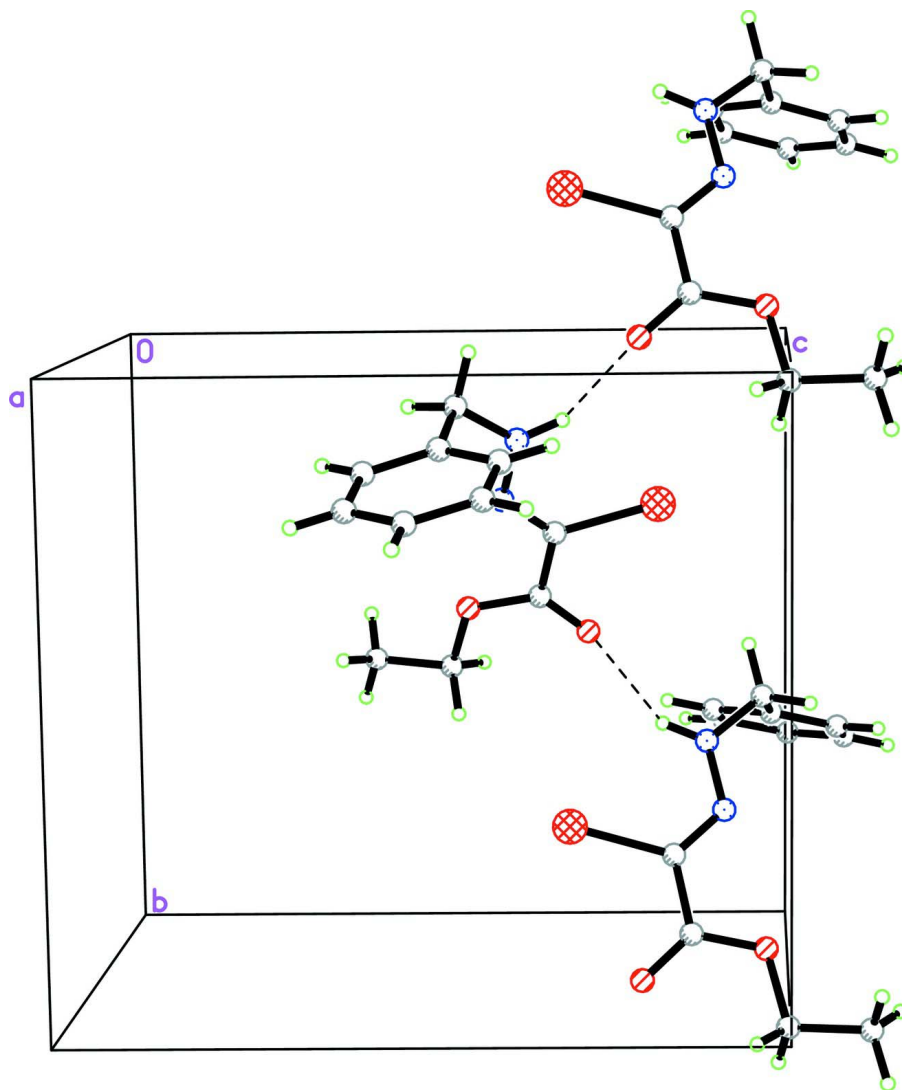


Figure 2

A view of the crystal structure of (I) showing chain to the *b* linked via N—H···O contact.

### Ethyl 2-[(*Z*)-2-benzylhydrazin-1-ylidene]-2-bromoacetate

#### Crystal data

$C_{11}H_{13}BrN_2O_2$

$M_r = 285.14$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2_1ybc$

$a = 9.046\ (1)\ \text{\AA}$

$b = 11.235\ (1)\ \text{\AA}$

$c = 12.326\ (2)\ \text{\AA}$

$\beta = 92.935\ (4)^\circ$

$V = 1251.1\ (3)\ \text{\AA}^3$

$Z = 4$

$F(000) = 576$

$D_x = 1.514\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1479 reflections

$\theta = 2.3\text{--}24.8^\circ$

$\mu = 3.27\ \text{mm}^{-1}$

$T = 294\ \text{K}$

Block, colorless

$0.25 \times 0.14 \times 0.07\ \text{mm}$

*Data collection*

|  |  |
|--|--|
| Bruker APEX CCD diffractometer                               | 4952 measured reflections  |
| Radiation source: fine-focus sealed tube                     | 2188 independent reflections   |
| Graphite monochromator                                       | 1475 reflections with $I > 2\sigma(I)$                                 |
| phi and $\omega$ scans                                       | $R_{\text{int}} = 0.019$   |
| Absorption correction: multi-scan<br>(SADABS; Siemens, 1996) | $\theta_{\text{max}} = 25.0^\circ$ , $\theta_{\text{min}} = 2.3^\circ$ |
| $T_{\text{min}} = 0.495$ , $T_{\text{max}} = 0.803$          | $h = -10 \rightarrow 10$   |
|  | $k = -13 \rightarrow 7$  |
|  | $l = -7 \rightarrow 14$  |

*Refinement*

|  |  |
|--|--|
| Refinement on $F^2$  | Secondary atom site location: difference Fourier map         |
| Least-squares matrix: full                                     | Hydrogen site location: inferred from neighbouring sites     |
| $R[F^2 > 2\sigma(F^2)] = 0.038$                                | H-atom parameters constrained                                |
| $wR(F^2) = 0.111$  | $w = 1/[\sigma^2(F_o^2) + (0.0656P)^2]$                      |
| $S = 1.02$   | where $P = (F_o^2 + 2F_c^2)/3$                               |
| 2188 reflections   | $(\Delta/\sigma)_{\text{max}} < 0.001$                       |
| 146 parameters   | $\Delta\rho_{\text{max}} = 0.26 \text{ e } \text{\AA}^{-3}$  |
| 0 restraints   | $\Delta\rho_{\text{min}} = -0.61 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods |  |

*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 ( $\text{\AA}^2$ )*

|     | $x$         | $y$         | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|--------------|----------------------------------|
| Br1 | 0.44688 (4) | 0.25237 (4) | 0.31304 (3)  | 0.0668 (2)                       |
| O1  | 0.3161 (3)  | 0.0317 (2)  | 0.2073 (2)   | 0.0755 (8)                       |
| O2  | 0.3458 (2)  | 0.0749 (2)  | 0.03230 (18) | 0.0534 (6)                       |
| N1  | 0.5769 (3)  | 0.3675 (3)  | 0.1176 (2)   | 0.0501 (7)                       |
| H1  | 0.5721      | 0.3973      | 0.1815       | 0.060*                           |
| N2  | 0.5071 (3)  | 0.2673 (2)  | 0.0922 (2)   | 0.0424 (7)                       |
| C1  | 0.8144 (3)  | 0.3760 (3)  | 0.0231 (3)   | 0.0436 (8)                       |
| C2  | 0.8605 (4)  | 0.3447 (4)  | -0.0771 (3)  | 0.0726 (11)                      |
| H2  | 0.7946      | 0.3505      | -0.1374      | 0.087*                           |
| C3  | 1.0035 (5)  | 0.3045 (4)  | -0.0906 (4)  | 0.0852 (13)                      |
| H3  | 1.0321      | 0.2834      | -0.1594      | 0.102*                           |
| C4  | 1.1013 (4)  | 0.2958 (4)  | -0.0045 (4)  | 0.0696 (11)                      |
| H4  | 1.1976      | 0.2700      | -0.0136      | 0.083*                           |
| C5  | 1.0569 (4)  | 0.3253 (4)  | 0.0954 (4)   | 0.0830 (13)                      |
| H5  | 1.1234      | 0.3182      | 0.1551       | 0.100*                           |
| C6  | 0.9142 (4)  | 0.3659 (4)  | 0.1105 (3)   | 0.0721 (11)                      |

|      |            |             |             |             |
|------|------------|-------------|-------------|-------------|
| H6   | 0.8863     | 0.3862      | 0.1797      | 0.087*      |
| C7   | 0.6617 (3) | 0.4268 (3)  | 0.0367 (3)  | 0.0475 (8)  |
| H7A  | 0.6717     | 0.5101      | 0.0563      | 0.057*      |
| H7B  | 0.6064     | 0.4228      | -0.0327     | 0.057*      |
| C8   | 0.4424 (3) | 0.2069 (3)  | 0.1640 (3)  | 0.0432 (7)  |
| C9   | 0.3625 (3) | 0.0958 (3)  | 0.1382 (3)  | 0.0508 (8)  |
| C10  | 0.2617 (4) | -0.0317 (4) | 0.0018 (3)  | 0.0722 (11) |
| H10A | 0.1758     | -0.0378     | 0.0454      | 0.087*      |
| H10B | 0.3226     | -0.1017     | 0.0151      | 0.087*      |
| C11  | 0.2142 (5) | -0.0254 (4) | -0.1139 (3) | 0.0950 (15) |
| H11A | 0.1489     | 0.0412      | -0.1259     | 0.142*      |
| H11B | 0.1632     | -0.0974     | -0.1349     | 0.142*      |
| H11C | 0.2993     | -0.0159     | -0.1565     | 0.142*      |

*Atomic displacement parameters (Å<sup>2</sup>)*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$      | $U^{13}$     | $U^{23}$      |
|-----|-------------|-------------|-------------|---------------|--------------|---------------|
| Br1 | 0.0724 (3)  | 0.0882 (4)  | 0.0405 (3)  | -0.00890 (18) | 0.00985 (18) | -0.00325 (18) |
| O1  | 0.1002 (19) | 0.0639 (19) | 0.0630 (17) | -0.0140 (15)  | 0.0091 (14)  | 0.0199 (14)   |
| O2  | 0.0622 (13) | 0.0418 (15) | 0.0561 (14) | -0.0035 (11)  | 0.0025 (11)  | -0.0015 (11)  |
| N1  | 0.0508 (14) | 0.0531 (19) | 0.0473 (16) | -0.0048 (13)  | 0.0106 (12)  | -0.0090 (14)  |
| N2  | 0.0409 (13) | 0.0448 (19) | 0.0414 (15) | 0.0058 (12)   | 0.0014 (12)  | -0.0029 (12)  |
| C1  | 0.0470 (16) | 0.0314 (19) | 0.053 (2)   | -0.0016 (13)  | 0.0059 (15)  | 0.0020 (16)   |
| C2  | 0.063 (2)   | 0.099 (3)   | 0.056 (2)   | 0.012 (2)     | 0.0053 (18)  | 0.000 (2)     |
| C3  | 0.080 (3)   | 0.104 (4)   | 0.074 (3)   | 0.021 (3)     | 0.024 (2)    | -0.012 (3)    |
| C4  | 0.055 (2)   | 0.057 (3)   | 0.099 (4)   | 0.0130 (18)   | 0.022 (2)    | 0.011 (2)     |
| C5  | 0.059 (2)   | 0.110 (4)   | 0.079 (3)   | 0.022 (2)     | -0.005 (2)   | 0.015 (3)     |
| C6  | 0.061 (2)   | 0.099 (3)   | 0.056 (2)   | 0.013 (2)     | 0.0058 (19)  | 0.001 (2)     |
| C7  | 0.0470 (17) | 0.041 (2)   | 0.055 (2)   | 0.0042 (14)   | 0.0064 (15)  | 0.0036 (16)   |
| C8  | 0.0423 (16) | 0.048 (2)   | 0.0393 (18) | 0.0079 (14)   | 0.0031 (14)  | 0.0039 (15)   |
| C9  | 0.0520 (18) | 0.049 (2)   | 0.051 (2)   | 0.0064 (15)   | 0.0036 (15)  | 0.0049 (18)   |
| C10 | 0.090 (3)   | 0.046 (3)   | 0.080 (3)   | -0.014 (2)    | 0.003 (2)    | -0.009 (2)    |
| C11 | 0.114 (4)   | 0.069 (3)   | 0.099 (4)   | -0.014 (3)    | -0.026 (3)   | -0.008 (3)    |

*Geometric parameters (Å, °)*

|        |           |          |           |
|--------|-----------|----------|-----------|
| Br1—C8 | 1.906 (3) | C4—C5    | 1.355 (6) |
| O1—C9  | 1.207 (4) | C4—H4    | 0.9300    |
| O2—C9  | 1.328 (4) | C5—C6    | 1.391 (5) |
| O2—C10 | 1.457 (4) | C5—H5    | 0.9300    |
| N1—N2  | 1.320 (3) | C6—H6    | 0.9300    |
| N1—C7  | 1.451 (4) | C7—H7A   | 0.9700    |
| N1—H1  | 0.8600    | C7—H7B   | 0.9700    |
| N2—C8  | 1.280 (4) | C8—C9    | 1.468 (5) |
| C1—C2  | 1.370 (4) | C10—C11  | 1.470 (5) |
| C1—C6  | 1.374 (5) | C10—H10A | 0.9700    |
| C1—C7  | 1.512 (4) | C10—H10B | 0.9700    |
| C2—C3  | 1.388 (5) | C11—H11A | 0.9600    |

|           |           |               |           |
|-----------|-----------|---------------|-----------|
| C2—H2     | 0.9300    | C11—H11B      | 0.9600    |
| C3—C4     | 1.350 (6) | C11—H11C      | 0.9600    |
| C3—H3     | 0.9300    |               |           |
| C9—O2—C10 | 115.5 (3) | N1—C7—H7A     | 108.5     |
| N2—N1—C7  | 119.5 (3) | C1—C7—H7A     | 108.5     |
| N2—N1—H1  | 120.2     | N1—C7—H7B     | 108.5     |
| C7—N1—H1  | 120.2     | C1—C7—H7B     | 108.5     |
| C8—N2—N1  | 121.2 (3) | H7A—C7—H7B    | 107.5     |
| C2—C1—C6  | 117.9 (3) | N2—C8—C9      | 122.6 (3) |
| C2—C1—C7  | 121.2 (3) | N2—C8—Br1     | 122.4 (3) |
| C6—C1—C7  | 120.7 (3) | C9—C8—Br1     | 115.0 (2) |
| C1—C2—C3  | 121.3 (4) | O1—C9—O2      | 124.2 (3) |
| C1—C2—H2  | 119.4     | O1—C9—C8      | 122.7 (3) |
| C3—C2—H2  | 119.4     | O2—C9—C8      | 113.1 (3) |
| C4—C3—C2  | 120.5 (4) | O2—C10—C11    | 109.5 (3) |
| C4—C3—H3  | 119.7     | O2—C10—H10A   | 109.8     |
| C2—C3—H3  | 119.7     | C11—C10—H10A  | 109.8     |
| C3—C4—C5  | 118.9 (4) | O2—C10—H10B   | 109.8     |
| C3—C4—H4  | 120.6     | C11—C10—H10B  | 109.8     |
| C5—C4—H4  | 120.6     | H10A—C10—H10B | 108.2     |
| C4—C5—C6  | 121.5 (4) | C10—C11—H11A  | 109.5     |
| C4—C5—H5  | 119.3     | C10—C11—H11B  | 109.5     |
| C6—C5—H5  | 119.3     | H11A—C11—H11B | 109.5     |
| C1—C6—C5  | 119.9 (4) | C10—C11—H11C  | 109.5     |
| C1—C6—H6  | 120.1     | H11A—C11—H11C | 109.5     |
| C5—C6—H6  | 120.1     | H11B—C11—H11C | 109.5     |
| N1—C7—C1  | 114.9 (3) |               |           |

*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> |
|--------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1 $\cdots$ O1 <sup>i</sup> | 0.86        | 2.24                | 2.965 (4)                  | 141                           |

Symmetry code: (i)  $-x+1, y+1/2, -z+1/2$ .