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Ethyl 6-methyl-8-phenyl-1,2,4-triazolo[1,5-*a*]pyridine-7-carboxylate

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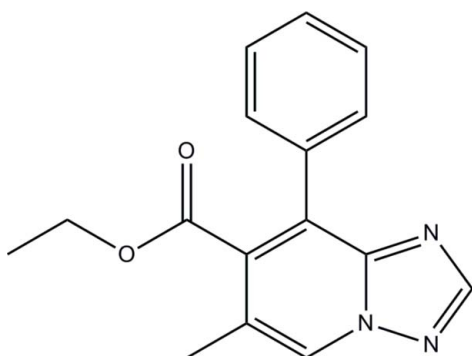
Received 29 October 2013; accepted 13 November 2013

Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.049; wR factor = 0.152; data-to-parameter ratio = 13.6.

In title compound, $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$, the 1,2,4-triazolo[1,5-*a*]pyridine ring system is almost planar (r.m.s. deviation = 0.0068 Å) and forms a dihedral angle of 61.4 (3)° with the phenyl ring. In the structure, centrosymmetrically related molecules are linked into dimers by pairs of $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds.

Related literature

For application of [1,2,4]triazolo[1,5-*a*]pyridine derivatives, see: Luo & Hu (2006); Liu & Hu (2002). For the synthesis of [1,2,4]triazolo[1,5-*a*]pyridine derivatives, see: Jones & Sliskovic (1983); Wang *et al.* (2003); Ge *et al.* (2009); Jia *et al.* (2010). For standard bond lengths, see: Allen *et al.* (1987).



Experimental

Crystal data

 $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$ $M_r = 281.31$

Monoclinic, $P2_1/n$
 $a = 13.401$ (3) Å
 $b = 7.4825$ (19) Å
 $c = 15.068$ (4) Å
 $\beta = 98.986$ (4)°
 $V = 1492.4$ (7) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 298$ K
 $0.23 \times 0.19 \times 0.15$ mm

Data collection

Brucker SMART APEXII CCD
 area-detector diffractometer
 Absorption correction: multi-scan
 (SADABS; Bruker, 1999)
 $T_{\min} = 0.981$, $T_{\max} = 0.987$

7312 measured reflections
 2611 independent reflections
 1920 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.086$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.152$
 $S = 1.05$
 2611 reflections

192 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.22$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{C6}-\text{H6}\cdots\text{N2}^i$ | 0.93 | 2.49 | 3.332 (3) | 151 |

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

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT (Bruker, 1999); 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 (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ5092).

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supplementary materials

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Ethyl 6-methyl-8-phenyl-1,2,4-triazolo[1,5-*a*]pyridine-7-carboxylate**Yang Li, Chen Sun and Ran Zhang****1. Comment**

[1,2,4]Triazolo[1,5-*a*]pyridine derivatives are important heterocyclic compounds which exhibit antifungal, anticancer and anti-inflammatory activities (Luo & Hu, 2006; Liu & Hu, 2002). Despite possessing outstanding biological activities, only a few [1,2,4]triazolo[1,5-*a*]pyridines are known. Some commonly used synthetic methods are the annulation of the 1,2,4-triazole ring starting with amino substituted pyridines by a multistep procedure (Jones & Sliskovic, 1983). Previously, imidazo[1,5-*a*]pyridines, pyrazolo[1,5-*a*]pyridines, imidazo[1,2-*a*]pyridines and indolizines had been synthesized by a novel tandem reaction in our group (Wang *et al.*, 2003; Ge *et al.*, 2009; Jia *et al.*, 2010). As an extension of this work, the synthesis of [1,2,4]triazolo[1,5-*a*]pyridine heterocycles through this procedure has been undertaken. We present here the crystal structure of one of such compounds, ethyl 8-phenyl-6-methyl-[1,2,4]triazolo[1,5-*a*]pyridine-7-carboxylate.

In title compound (Fig. 1) the the [1,2,4]triazolo[1,5-*a*]pyridine ring system is almost planar, as indicated by its r.m.s. deviation of 0.0068 Å and by the dihedral angle of 0.9 (3)° between the pyridine and triazole rings. The C10–C15 phenyl ring is tilted by 61.4 (3)° with respect to the mean plane through the fused-ring system. All bond lengths (Allen *et al.*, 1987) and angles in the molecule are normal. In the crystal structure, centrosymmetrically related molecules form dimeric units by a pair of C—H⋯N intermolecular hydrogen bonds (Table 1).

2. Experimental

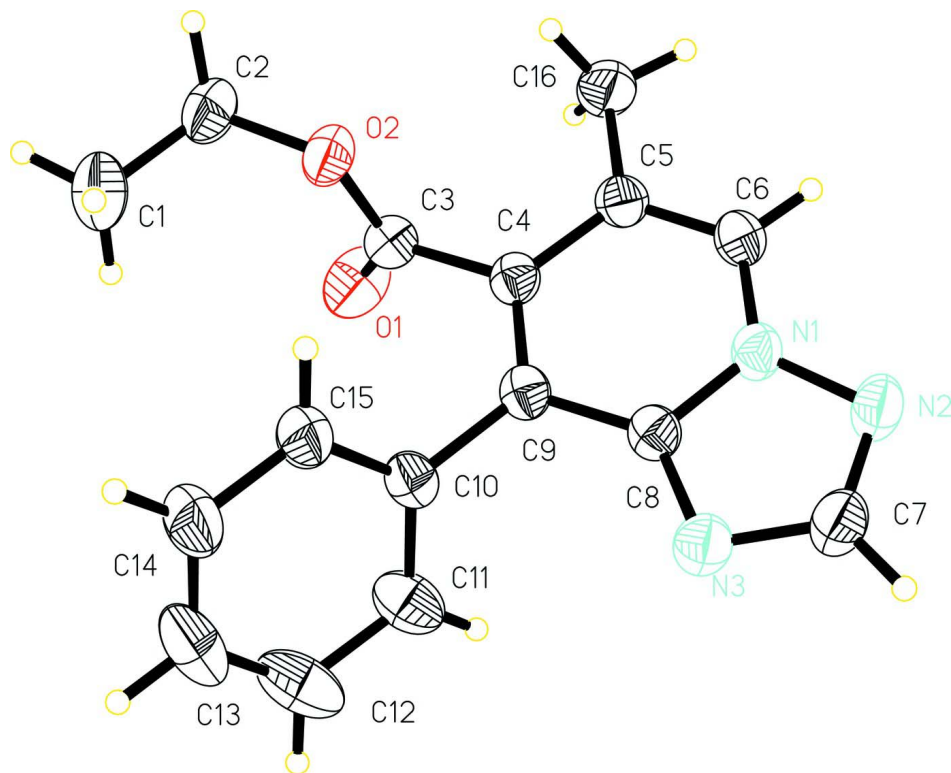
Phenyl(1*H*-1,2,4-triazol-5-yl)methanone (6 mmol), ethyl 4-bromo-3-methylbut-2-enoate (12 mmol), potassium carbonate (1.8 g, 13.2 mmol) and DMF (30 ml) were added to a 100 ml round-bottomed flask and stirred for 8 h. The mixture was then poured into water (200 ml) and extracted with dichloromethane (3 × 50 ml). The organic layers were combined and dried over anhydrous Na₂SO₄, then filtered, and the mixture concentrated by rotary evaporation. The crude products were depurated by using column chromatography in 72% isolated yield. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the title compound in a hexane/ethyl acetate mixture (3:1 v/v) at room temperature over a period of one week.

3. Refinement

All H atoms were found on a difference Fourier map, with C—H = 0.93–0.97 Å and included in the final cycles of refinement using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Computing details

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE* (Bruker, 1999); 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* (Sheldrick, 2008).

**Figure 1**

The molecular structure of the title compounds, with displacement ellipsoids drawn at the 30% probability level.

Ethyl 6-methyl-8-phenyl-1,2,4-triazolo[1,5-a]pyridine-7-carboxylate

Crystal data

$C_{16}H_{15}N_3O_2$

$M_r = 281.31$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 13.401\ (3)\ \text{\AA}$

$b = 7.4825\ (19)\ \text{\AA}$

$c = 15.068\ (4)\ \text{\AA}$

$\beta = 98.986\ (4)^\circ$

$V = 1492.4\ (7)\ \text{\AA}^3$

$Z = 4$

$F(000) = 592$

$D_x = 1.252\ \text{Mg m}^{-3}$

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

Cell parameters from 3034 reflections

$\theta = 2.7\text{--}25.1^\circ$

$\mu = 0.09\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Block, colourless

$0.23 \times 0.19 \times 0.15\ \text{mm}$

Data collection

Brucker SMART APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ϕ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 1999)

$T_{\min} = 0.981$, $T_{\max} = 0.987$

7312 measured reflections

2611 independent reflections

1920 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.086$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 1.9^\circ$

$h = -10 \rightarrow 15$

$k = -8 \rightarrow 7$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.152$
 $S = 1.05$
 2611 reflections
 192 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
 $w = 1/[\sigma^2(F_o^2) + (0.073P)^2 + 0.2662P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

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)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| N1 | 0.10885 (12) | 0.7854 (2) | 0.55820 (10) | 0.0547 (4) |
| N2 | 0.09507 (14) | 0.9165 (2) | 0.61803 (11) | 0.0672 (5) |
| N3 | 0.23653 (13) | 0.7566 (2) | 0.66890 (10) | 0.0628 (5) |
| O1 | 0.25306 (14) | 0.4080 (2) | 0.34386 (12) | 0.0912 (6) |
| O2 | 0.14672 (10) | 0.22579 (18) | 0.39941 (9) | 0.0636 (4) |
| C1 | 0.2563 (2) | -0.0255 (4) | 0.3838 (2) | 0.0930 (8) |
| H1A | 0.3166 | 0.0453 | 0.3874 | 0.140* |
| H1B | 0.2629 | -0.1306 | 0.3486 | 0.140* |
| H1C | 0.2463 | -0.0598 | 0.4432 | 0.140* |
| C2 | 0.16849 (19) | 0.0806 (3) | 0.34085 (16) | 0.0752 (6) |
| H2A | 0.1827 | 0.1295 | 0.2845 | 0.090* |
| H2B | 0.1098 | 0.0035 | 0.3278 | 0.090* |
| C3 | 0.19373 (14) | 0.3795 (3) | 0.39345 (12) | 0.0555 (5) |
| C4 | 0.16236 (13) | 0.5171 (2) | 0.45608 (12) | 0.0499 (5) |
| C5 | 0.07336 (14) | 0.6198 (3) | 0.42544 (13) | 0.0556 (5) |
| C6 | 0.04891 (14) | 0.7524 (3) | 0.47858 (13) | 0.0589 (5) |
| H6 | -0.0087 | 0.8208 | 0.4609 | 0.071* |
| C7 | 0.17325 (18) | 0.8910 (3) | 0.68132 (14) | 0.0687 (6) |
| H7 | 0.1843 | 0.9626 | 0.7324 | 0.082* |
| C8 | 0.19436 (14) | 0.6907 (2) | 0.58965 (12) | 0.0509 (5) |
| C9 | 0.22271 (13) | 0.5487 (2) | 0.53631 (12) | 0.0488 (5) |
| C10 | 0.31516 (14) | 0.4442 (3) | 0.57064 (12) | 0.0541 (5) |
| C11 | 0.40784 (15) | 0.5273 (4) | 0.58803 (16) | 0.0791 (7) |
| H11 | 0.4132 | 0.6496 | 0.5789 | 0.095* |
| C14 | 0.3930 (2) | 0.1653 (4) | 0.62015 (18) | 0.0902 (8) |
| H14 | 0.3876 | 0.0438 | 0.6315 | 0.108* |

| | | | | |
|------|--------------|------------|--------------|-------------|
| C15 | 0.30836 (17) | 0.2630 (3) | 0.58754 (14) | 0.0698 (6) |
| H15 | 0.2457 | 0.2068 | 0.5767 | 0.084* |
| C16 | 0.01047 (17) | 0.5868 (3) | 0.33544 (15) | 0.0759 (7) |
| H16A | -0.0466 | 0.6659 | 0.3276 | 0.114* |
| H16B | -0.0127 | 0.4652 | 0.3322 | 0.114* |
| H16C | 0.0505 | 0.6081 | 0.2889 | 0.114* |
| C12 | 0.49383 (18) | 0.4263 (5) | 0.61947 (19) | 0.1016 (10) |
| H12 | 0.5571 | 0.4802 | 0.6294 | 0.122* |
| C13 | 0.4843 (2) | 0.2469 (5) | 0.6356 (2) | 0.1015 (10) |
| H13 | 0.5414 | 0.1804 | 0.6575 | 0.122* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| N1 | 0.0617 (9) | 0.0450 (9) | 0.0561 (9) | 0.0084 (7) | 0.0047 (7) | 0.0023 (7) |
| N2 | 0.0850 (12) | 0.0518 (10) | 0.0632 (10) | 0.0147 (9) | 0.0069 (9) | -0.0068 (8) |
| N3 | 0.0732 (11) | 0.0605 (10) | 0.0531 (9) | 0.0066 (9) | 0.0045 (8) | -0.0003 (8) |
| O1 | 0.1124 (13) | 0.0857 (12) | 0.0881 (11) | -0.0218 (10) | 0.0553 (10) | -0.0121 (9) |
| O2 | 0.0725 (9) | 0.0494 (8) | 0.0730 (9) | -0.0023 (7) | 0.0240 (7) | -0.0091 (6) |
| C1 | 0.1027 (18) | 0.0772 (17) | 0.1035 (19) | 0.0237 (15) | 0.0294 (16) | -0.0102 (15) |
| C2 | 0.0908 (16) | 0.0612 (13) | 0.0759 (14) | 0.0012 (12) | 0.0202 (12) | -0.0175 (11) |
| C3 | 0.0584 (11) | 0.0556 (12) | 0.0530 (10) | -0.0017 (9) | 0.0102 (9) | 0.0014 (9) |
| C4 | 0.0528 (10) | 0.0442 (10) | 0.0535 (10) | -0.0008 (8) | 0.0106 (8) | 0.0044 (8) |
| C5 | 0.0560 (11) | 0.0505 (11) | 0.0581 (11) | 0.0009 (9) | 0.0023 (9) | 0.0046 (9) |
| C6 | 0.0580 (11) | 0.0506 (11) | 0.0649 (12) | 0.0104 (9) | -0.0006 (9) | 0.0054 (10) |
| C7 | 0.0871 (15) | 0.0588 (13) | 0.0587 (12) | 0.0090 (12) | 0.0066 (11) | -0.0063 (10) |
| C8 | 0.0558 (10) | 0.0467 (10) | 0.0494 (10) | 0.0031 (8) | 0.0059 (8) | 0.0071 (8) |
| C9 | 0.0520 (10) | 0.0450 (10) | 0.0505 (10) | 0.0019 (8) | 0.0112 (8) | 0.0073 (8) |
| C10 | 0.0541 (10) | 0.0622 (12) | 0.0462 (10) | 0.0089 (9) | 0.0087 (8) | 0.0030 (8) |
| C11 | 0.0578 (13) | 0.0981 (18) | 0.0817 (15) | -0.0013 (12) | 0.0118 (11) | 0.0211 (14) |
| C14 | 0.0914 (19) | 0.0786 (17) | 0.0925 (17) | 0.0314 (15) | -0.0107 (14) | 0.0037 (14) |
| C15 | 0.0719 (13) | 0.0598 (13) | 0.0730 (14) | 0.0130 (11) | -0.0034 (11) | 0.0006 (11) |
| C16 | 0.0772 (14) | 0.0723 (15) | 0.0710 (13) | 0.0060 (12) | -0.0106 (11) | -0.0051 (11) |
| C12 | 0.0531 (13) | 0.161 (3) | 0.0913 (18) | 0.0025 (17) | 0.0116 (12) | 0.0282 (19) |
| C13 | 0.0799 (19) | 0.127 (3) | 0.0966 (19) | 0.0475 (19) | 0.0126 (15) | 0.0175 (19) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------|-----------|---------|-----------|
| N1—C6 | 1.358 (2) | C5—C16 | 1.501 (3) |
| N1—N2 | 1.364 (2) | C6—H6 | 0.9300 |
| N1—C8 | 1.368 (2) | C7—H7 | 0.9300 |
| N2—C7 | 1.316 (3) | C8—C9 | 1.420 (3) |
| N3—C8 | 1.333 (2) | C9—C10 | 1.488 (2) |
| N3—C7 | 1.347 (3) | C10—C11 | 1.377 (3) |
| O1—C3 | 1.192 (2) | C10—C15 | 1.385 (3) |
| O2—C3 | 1.322 (2) | C11—C12 | 1.397 (4) |
| O2—C2 | 1.458 (2) | C11—H11 | 0.9300 |
| C1—C2 | 1.482 (3) | C14—C13 | 1.355 (4) |
| C1—H1A | 0.9600 | C14—C15 | 1.374 (3) |
| C1—H1B | 0.9600 | C14—H14 | 0.9300 |

| | | | |
|------------|-------------|---------------|-------------|
| C1—H1C | 0.9600 | C15—H15 | 0.9300 |
| C2—H2A | 0.9700 | C16—H16A | 0.9600 |
| C2—H2B | 0.9700 | C16—H16B | 0.9600 |
| C3—C4 | 1.500 (3) | C16—H16C | 0.9600 |
| C4—C9 | 1.366 (3) | C12—C13 | 1.374 (5) |
| C4—C5 | 1.433 (3) | C12—H12 | 0.9300 |
| C5—C6 | 1.347 (3) | C13—H13 | 0.9300 |
| | | | |
| C6—N1—N2 | 126.33 (15) | N3—C7—H7 | 121.5 |
| C6—N1—C8 | 124.03 (16) | N3—C8—N1 | 109.50 (17) |
| N2—N1—C8 | 109.64 (15) | N3—C8—C9 | 132.10 (17) |
| C7—N2—N1 | 101.54 (16) | N1—C8—C9 | 118.40 (15) |
| C8—N3—C7 | 102.27 (16) | C4—C9—C8 | 117.18 (16) |
| C3—O2—C2 | 117.72 (16) | C4—C9—C10 | 124.22 (16) |
| C2—C1—H1A | 109.5 | C8—C9—C10 | 118.60 (15) |
| C2—C1—H1B | 109.5 | C11—C10—C15 | 119.36 (19) |
| H1A—C1—H1B | 109.5 | C11—C10—C9 | 120.41 (19) |
| C2—C1—H1C | 109.5 | C15—C10—C9 | 120.21 (18) |
| H1A—C1—H1C | 109.5 | C10—C11—C12 | 119.5 (3) |
| H1B—C1—H1C | 109.5 | C10—C11—H11 | 120.3 |
| O2—C2—C1 | 110.81 (19) | C12—C11—H11 | 120.3 |
| O2—C2—H2A | 109.5 | C13—C14—C15 | 119.6 (3) |
| C1—C2—H2A | 109.5 | C13—C14—H14 | 120.2 |
| O2—C2—H2B | 109.5 | C15—C14—H14 | 120.2 |
| C1—C2—H2B | 109.5 | C14—C15—C10 | 120.8 (2) |
| H2A—C2—H2B | 108.1 | C14—C15—H15 | 119.6 |
| O1—C3—O2 | 124.74 (19) | C10—C15—H15 | 119.6 |
| O1—C3—C4 | 123.47 (19) | C5—C16—H16A | 109.5 |
| O2—C3—C4 | 111.78 (15) | C5—C16—H16B | 109.5 |
| C9—C4—C5 | 122.70 (17) | H16A—C16—H16B | 109.5 |
| C9—C4—C3 | 119.35 (16) | C5—C16—H16C | 109.5 |
| C5—C4—C3 | 117.77 (16) | H16A—C16—H16C | 109.5 |
| C6—C5—C4 | 118.08 (17) | H16B—C16—H16C | 109.5 |
| C6—C5—C16 | 120.25 (18) | C13—C12—C11 | 119.6 (3) |
| C4—C5—C16 | 121.63 (18) | C13—C12—H12 | 120.2 |
| C5—C6—N1 | 119.61 (17) | C11—C12—H12 | 120.2 |
| C5—C6—H6 | 120.2 | C14—C13—C12 | 121.1 (2) |
| N1—C6—H6 | 120.2 | C14—C13—H13 | 119.4 |
| N2—C7—N3 | 117.05 (19) | C12—C13—H13 | 119.4 |
| N2—C7—H7 | 121.5 | | |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------|-------|-------------|-------------|---------------|
| C6—H6 \cdots N2 ⁱ | 0.93 | 2.49 | 3.332 (3) | 151 |

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