Ethyl 2-[4-(4-methoxybenzyl)-3-methyl-6-oxopyridazin-1-yl]acetate

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In the title molecule, C17H20N2O4, the inner part of the ester substituent is nearly perpendicular to the dihydropyridazine ring, forming a dihedral angle of 83.21 (7). In the crystal, inversion dimers are formed by pairwise C—H⋯O interactions with the dimers connected into chains extending along the b-axis direction by C—H⋯π(ring) interactions. The chains are connected by π-stacking interactions to give corrugated layers parallel to the ab plane. The terminal ethyl group is disordered over two two sets of sites with the major component having a site occupancy factor of 0.715 (10).

Received 26 May 2022
Accepted 30 May 2022

Edited by E. R. T. Tiekink, Sunway University, Malaysia

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Keywords: crystal structure; dihydropyridazine; hydrogen bond; π-stacking.

CCDC reference: 2175897

Structural data: full structural data are available from iucrdata.iucr.org

3D view

Chemical scheme

Structure description

Pyridazinone derivatives, with a carbonyl group at position 3, possess a number of biological activities including anti-oxidant (Khokra et al., 2016), anti-bacterial and anti-fungal (Abiha et al., 2018), anti-cancer (Kamble et al., 2017), analgesic and anti-inflammatory (Ibrahim et al., 2017), anti-depressant (Boukharsa et al., 2016) and anti-ulcer activities (Yamada et al., 1981). In addition, a number of pyridazinone derivatives have been reported to have potential as agrochemicals, for example as insecticides (Nauen & Bretschneider, 2002). As part of our ongoing studies of these systems, we report herein the synthesis and the molecular and crystal structure of the title compound (Fig. 1).

The dihedral angle between the N1/N2/C1–C4 and C6–C11 planes is 89.74 (3)° while that between the N1/N2/C1–C4 plane and that defined by N2/C14/C15/O3 is 83.21 (7)°. This latter angle indicates that the inner end of the substituent on N2 is nearly perpendicular to the tetrahydropyridazine ring. The C2—C3—C5—C6 torsion angle of −9.4 (2)° indicates that the centroid of the 4-methoxyphenyl ring is only slightly below...
the plane of the pyridazine ring. This conformation appears to be the result of the intermolecular π-stacking interaction (see below).

In the crystal, inversion dimers are formed by pairwise C14—H14⋯O1 interactions (Table 1) with the dimers connected into chains extending along the b-axis direction by C16—H16⋯Cg1 interactions (Table 1 and Fig. 2). The chains are connected to one another by π-stacking interactions between the N1/N2/C1–C4 and C6···C11 rings [symmetry code: (i) −x + 1, y, −z + 1/2; (ii) x, y, −1 + z] with a centroid–centroid distance of 3.8870 (8) Å and a dihedral angle of 7.29 (6)° to give corrugated layers parallel to the ab plane (Figs. 2 and 3).

**Synthesis and crystallization**

A mixture of 3-(4-methoxybenzylidene)-4-oxopentanoic acid (0.05 mol) and hydrazine hydrate (0.1 mol) in ethanol (100 ml) was refluxed for 2 h. The precipitate that formed was filtered off and recrystallized from acetone solution to obtain

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**Table 1**

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|-------|-----|-----|-----|-------|
| C14—H14B⋯O1i | 0.97 | 2.44 | 3.4041 (19) | 175 |
| C16—H16B⋯Cg1ii | 0.97 | 2.86 | 3.586 (3) | 132 |

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

**Table 2**

| Crystal data | Chemical formula | C17H20N2O4 | M_r | 316.35 |
|--------------|------------------|-------------|-----|--------|
| Crystal system, space group | Monoclinic, C2/c | | |
| Temperature (K) | 298 | |
| a, b, c (Å) | 23.0488 (9), 8.1149 (3), 18.3223 (7) | |
| β (°) | 104.454 (1) | |
| V (Å³) | 3318.5 (2) | |
| Z | 8 | |
| Radiation type | Mo Kα | |
| μ (mm⁻¹) | 0.09 | |
| Crystal size (mm) | 0.30 × 0.27 × 0.26 | |

**Figure 1**

The title molecule with labelling scheme and 30% probability ellipsoids. Only the major component of the disordered ethyl group is shown.

**Figure 2**

Detail of the intermolecular interactions viewed along the c-axis direction. C—H⋯O hydrogen bonds are shown by black dashed lines while π-stacking and C—H⋯π(ring) interactions are shown, respectively, by orange and green dashed lines.

**Figure 3**

Packing viewed along the b-axis direction with the highlighted intermolecular interactions shown as in Fig. 2.
the 5-(4-methoxybenzyl)-6-methylpyridazin-3(2H)-one precursor. To this pyridazine derivative (0.05 mol) was added potassium carbonate (0.1 mmol), tetrabutylammonium bromide (0.01 mmol) and 2-ethyl bromoacetate (0.1 mol) in dimethylformamide (20 ml). The mixture was stirred for 24 h at room temperature. At the end of the reaction, the solution was filtered and the solvent evaporated under reduced pressure. The residue was washed with water and methylene chloride. The solvent was removed and colourless blocks of the title compound were obtained by recrystallization of the product from its acetone solution.

Yield 79%; m.p. 406–408 K. IR (cm\(^{-1}\)): 1743 (C=O, CO\(_2\)Et), 1660 (C=ON), 1599 (C=C), 1205 (C–N), 1011 and 1145 (C–O, CO\(_2\)Et sym and asym). \(^1\)H NMR (p.p.m.): 1.23 (t, 3H, J = 7.1, CH\(_2\)-CH\(_3\)); 2.22 (s, 3H, CH\(_3\)-pyridazine); 2.33 (s, 3H, OCH\(_3\)-phenyl); 3.85 (s, 2H, phenyl-CH\(_2\)-pyridazine); 4.17 (q, 2H, J = 7.1, O—CH\(_2\)-CH\(_3\)); 4.87 (s, 2H, –N—CH\(_2\)-CO); 6.48 (s, 1H, pyridazine); 6.93–6.96 (d, 2H, J = 9, phenyl); 7.25–7.27 (d, 2H, J = 9, phenyl). \(^13\)C NMR (p.p.m.): 14.11 (CH\(_3\)); 21.03 (CH\(_3\), pyridazine); 25.21 (OCH\(_3\), phenyl); 37.67 (CH\(_2\)); 51.34 (CH\(_2\)); 60.95 (CH\(_3\)); 127.13–127.44 (CH aromatic); 129.13–130.35 (CH aromatic); 132.12 (C=Ca aromatic); 136.51 (CH\(_2\)-C= aromatic); 138.49 (CH, pyridazine); 144.97 (CH\(_3\)-C=CH, pyridazine); 147.17 (C=N); 161.19 (C=O, pyridazine); 169.52 (C=O, CO\(_2\)Et).

Refinement
Crystal data, data collection and structure refinement details are summarized in Table 2. The C16/C17 ethyl group is disordered and was refined as two components restrained to have comparable geometries. The refined occupancies were 0.715 (10) and 0.285 (10).

Acknowledgements
JTM thanks Tulane University for support of the Tulane Crystallography Laboratory. Author contributions are as follows. Conceptualization, MA and JT; methodology, YR; investigation, YZ and HA; writing (original draft), JMT and YR; writing (review and editing of the manuscript), YR; formal analysis, AS and YR; supervision, MA and YR; crystal structure determination and validation, JTM.

References
Abiha, G. B., Bahar, L. & Utku, S. (2018). Rev. Rom. Med. Lab. 26, 231–241.
Boukharsa, Y., Meddah, B., Tiendrebeogo, R. Y., Ibrahim, A., Taoufil, J., Cherrah, Y., Benomar, A., Faouzi, M. E. A. & Ansar, M. (2016). Med. Chem. Res. 25, 494–500.
Brandenburg, K. & Putz, H. (2012). DIAMOND, Crystal Impact GbR, Bonn, Germany.
Bruker (2016). APEX3 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Ibrahim, T. H., Loksha, Y. M., Elshihawy, H. A., Khodeer, D. M. & Said, M. M. (2017). Arch. Pharm. Chem. Life Sci. 350, e1700093.
Kamble, V. T., Sawant, A.-S., Sawant, S. S., Pisal, P. M., Gacche, R. N., Kamble, S. S., Shegokar, H. D. & Kamble, V. A. (2017). J. Basic Appl. Res. Int. 21, 10–39.
Khokra, S. L., Khan, S. A., Thakur, P., Chowdhary, D., Ahmad, A. & Husain, A. (2016). J. Chin. Chem. Soc. 63, 739–750.
Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3–10.
Nauen, R. & Bretschneider, T. (2002). Pest. Outlook, 13, 241–245.
Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.
Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.
Yamada, T., Nobuhara, Y., Shimamura, H., Yoshihira, K., Yama-guchi, A. & Ohki, M. (1981). Chem. Pharm. Bull. 29, 3433–3439.
full crystallographic data

*IUCrData* (2022). 7, x220582  [https://doi.org/10.1107/S241431462200582X]

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Ethyl 2-[4-(4-methoxybenzyl)-3-methyl-6-oxopyridazin-1-yl]acetate

Crystal data

\[ C_{17}H_{20}N_{2}O_{4} \]

\[ M_r = 316.35 \]

Monoclinic, \( C2/c \)

\[ a = 23.0488 \ (9) \ \text{Å} \]

\[ b = 8.1149 \ (3) \ \text{Å} \]

\[ c = 18.3223 \ (7) \ \text{Å} \]

\[ \beta = 104.454 \ (1)^\circ \]

\[ V = 3318.5 \ (2) \ \text{Å}^3 \]

\[ Z = 8 \]

Cell parameters from 9996 reflections

\[ \theta = 2.3–27.3^\circ \]

\[ \mu = 0.09 \ \text{mm}^{-1} \]

\[ T = 298 \ \text{K} \]

Block, colourless

\[ 0.30 \times 0.27 \times 0.26 \ \text{mm} \]

Data collection

Bruker SMART APEX CCD diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3333 pixels mm\(^{-1}\)

\( \varphi \) and \( \omega \) scans

\( \omega \) and \( \varphi \) scans

Absorption correction: multi-scan

\( \text{(SADABS; Krause et al., 2015)} \)

\[ \tilde{T}_{\text{min}} = 0.88, \tilde{T}_{\text{max}} = 0.98 \]

Refinement

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R(F^2 > 2\sigma(F^2)) = 0.048 \]

\[ wR(F^2) = 0.160 \]

\[ S = 1.11 \]

4288 reflections

217 parameters

26 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

\( \Delta \sigma(\Delta)_{\text{max}} = 0.001 \)

\( \Delta \rho_{\text{max}} = 0.28 \ \text{e} \ \text{Å}^{-3} \)

\( \Delta \rho_{\text{min}} = -0.19 \ \text{e} \ \text{Å}^{-3} \)

Special details

**Experimental.** The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5\(^\circ\) in \( \omega \), collected at \( \varphi = 0.00, 90.00 \) and 180.00\(^\circ\) and 2 sets of 800 frames, each of width 0.45\(^\circ\) in \( \varphi \), collected at \( \omega = -30.00 \) and 210.00\(^\circ\). The scan time was 20 sec/frame.
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 $F^2 > 2\sigma(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å). All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. The ethyl group in the ester is disordered over several closely spaced sites that could not be separated so a 2-site model with ISOR restraints on the two carbon atoms was used to approximate the disorder. The geometries of the two components were restrained to be similar.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

| Atom | $x$   | $y$    | $z$     | $U_{iso}$/$U_{eq}$ | Occ. (<1) |
|------|------|-------|--------|-------------------|-----------|
| O1   | 0.41842 (6) | 0.43017 (16) | 0.23630 (6) | 0.0793 (4) |           |
| O2   | 0.22537 (6) | 1.02992 (16) | −0.00750 (6) | 0.0805 (4) |           |
| O3   | 0.41772 (5) | 0.17898 (16) | 0.38013 (10) | 0.0912 (5) |           |
| O4   | 0.51197 (4) | 0.12696 (12) | 0.37673 (8) | 0.0698 (3) |           |
| N1   | 0.42422 (5) | 0.60597 (13) | 0.41467 (6) | 0.0471 (3) |           |
| N2   | 0.43660 (5) | 0.51627 (13) | 0.35755 (6) | 0.0486 (3) |           |
| C1   | 0.40601 (6) | 0.52488 (17) | 0.28277 (8) | 0.0535 (3) |           |
| C2   | 0.36172 (6) | 0.65291 (17) | 0.26634 (7) | 0.0509 (3) |           |
| H2   | 0.340914 | 0.670615 | 0.216534 | 0.061* |           |
| C3   | 0.34933 (5) | 0.74800 (14) | 0.32046 (6) | 0.0426 (3) |           |
| C4   | 0.38196 (5) | 0.71634 (15) | 0.39722 (6) | 0.0438 (3) |           |
| C5   | 0.30371 (6) | 0.88585 (16) | 0.30417 (7) | 0.0517 (3) |           |
| H5A  | 0.270037 | 0.855686 | 0.324288 | 0.062* |           |
| H5B  | 0.321688 | 0.984256 | 0.330396 | 0.062* |           |
| C6   | 0.28079 (6) | 0.92540 (15) | 0.22187 (7) | 0.0455 (3) |           |
| C7   | 0.23054 (6) | 0.84826 (17) | 0.17780 (8) | 0.0539 (3) |           |
| H7   | 0.209482 | 0.774610 | 0.200416 | 0.065* |           |
| C8   | 0.21068 (6) | 0.87733 (18) | 0.10115 (8) | 0.0574 (3) |           |
| H8   | 0.177154 | 0.822651 | 0.072685 | 0.069* |           |
| C9   | 0.24120 (7) | 0.98837 (17) | 0.06746 (8) | 0.0544 (3) |           |
| C10  | 0.29086 (7) | 1.06967 (19) | 0.11082 (8) | 0.0570 (3) |           |
| C11  | 0.301934 | 1.146522 | 0.088495 | 0.068* |           |
| C12  | 0.31060 (6) | 1.03723 (17) | 0.18676 (8) | 0.0502 (3) |           |
| C13  | 0.344438 | 1.091021 | 0.214985 | 0.060* |           |
| C12  | 0.17493 (11) | 0.9506 (3) | −0.05390 (11) | 0.0984 (7) |           |
| H12A | 0.166108 | 0.998274 | −0.0103401 | 0.148* |           |
| H12B | 0.141106 | 0.964302 | −0.032724 | 0.148* |           |
| H12C | 0.183288 | 0.835300 | −0.057109 | 0.148* |           |
| C13  | 0.36960 (7) | 0.81397 (19) | 0.46090 (7) | 0.0582 (4) |           |
| H13A | 0.327840 | 0.805916 | 0.459828 | 0.087* |           |
| H13B | 0.379875 | 0.927322 | 0.455881 | 0.087* |           |
| H13C | 0.393143 | 0.771336 | 0.507866 | 0.087* |           |
| X      | Y      | Z      | U11   | U22   | U33   | U12   | U13   | U23   |
|--------|--------|--------|-------|-------|-------|-------|-------|-------|-------|
| O1     | 0.0871 | 0.0886 | 0.0579 | 0.0359 | 0.0098 | -0.0166 |       |       |       |
| O2     | 0.1027 | 0.0890 | 0.0432 | 0.0049 | 0.0060 | 0.0026  |       |       |       |
| O3     | 0.0543 | 0.0670 | 0.1584 | 0.0010 | 0.0278 | 0.0212  |       |       |       |
| O4     | 0.0504 | 0.0479 | 0.1109 | 0.0018 | 0.0199 | -0.0016 |       |       |       |
| N1     | 0.0496 | 0.0486 | 0.0416 | -0.0019 | 0.0085 | 0.0021  |       |       |       |
| N2     | 0.0494 | 0.0477 | 0.0465 | 0.0068 | 0.0079 | 0.0020  |       |       |       |
| C1     | 0.0559 | 0.0569 | 0.0467 | 0.0103 | 0.0107 | -0.0031 |       |       |       |
| C2     | 0.0572 | 0.0545 | 0.0382 | 0.0099 | 0.0067 | 0.0000  |       |       |       |
| C3     | 0.0457 | 0.0419 | 0.0403 | 0.0004 | 0.0109 | 0.0030  |       |       |       |
| C4     | 0.0481 | 0.0452 | 0.0382 | -0.0033 | 0.0113 | 0.0016  |       |       |       |
| C5     | 0.0603 | 0.0492 | 0.0466 | 0.0110 | 0.0150 | 0.0022  |       |       |       |
| C6     | 0.0479 | 0.0420 | 0.0468 | 0.0087 | 0.0125 | 0.0032  |       |       |       |
| C7     | 0.0512 | 0.0477 | 0.0618 | -0.0010 | 0.0120 | 0.0075  |       |       |       |
| C8     | 0.0497 | 0.0550 | 0.0604 | 0.0004 | 0.0002 | -0.0032 |       |       |       |
| C9     | 0.0619 | 0.0554 | 0.0445 | 0.0104 | 0.0103 | 0.0008  |       |       |       |
| C10    | 0.0625 | 0.0588 | 0.0531 | -0.0039 | 0.0210 | 0.0047  |       |       |       |
| C11    | 0.0460 | 0.0532 | 0.0514 | -0.0034 | 0.0120 | -0.0023 |       |       |       |
| C12    | 0.1217 | 0.0963 | 0.0571 | 0.0208 | -0.0154 | -0.0184 |       |       |       |
| C13    | 0.0673 | 0.0600 | 0.0411 | 0.0043 | 0.0130 | -0.0044 |       |       |       |
| C14    | 0.0451 | 0.0519 | 0.0578 | 0.0046 | 0.0064 | 0.0050  |       |       |       |
| C15    | 0.0469 | 0.0528 | 0.0662 | 0.0044 | 0.0112 | 0.0040  |       |       |       |
| C16    | 0.0679 | 0.0496 | 0.1000 | -0.0014 | 0.0153 | 0.0002  |       |       |       |
| C17    | 0.0807 | 0.0606 | 0.1594 | 0.0052 | 0.0223 | -0.0183 |       |       |       |
| C16A   | 0.0679 | 0.0496 | 0.1000 | -0.0014 | 0.0153 | 0.0002  |       |       |       |
| C17A   | 0.0807 | 0.0606 | 0.1594 | 0.0052 | 0.0223 | -0.0183 |       |       |       |

**Atomic displacement parameters (Å²)**

| X      | Y      | Z      | U11   | U22   | U33   | U12   | U13   | U23   |
|--------|--------|--------|-------|-------|-------|-------|-------|-------|-------|
| C14    | 0.4866 | 0.4023 | 0.3789 | 0.0528 |       |       |       |       |       |
| H14A   | 0.5103 | 0.4297 | 0.4287 | 0.063  |       |       |       |       |       |
| H14B   | 0.5119 | 0.4145 | 0.3439 | 0.063  |       |       |       |       |       |
| C15    | 0.4667 | 0.2259 | 0.3781 | 0.0558 |       |       |       |       |       |
| C16    | 0.5027 | -0.0502| 0.3871 | 0.0734 | 0.715 |       |       |       |       |
| H16A   | 0.4948 | -0.0689| 0.4360 | 0.088  | 0.715 |       |       |       |       |
| H16B   | 0.4682 | -0.0885| 0.3487 | 0.088  | 0.715 |       |       |       |       |
| C17    | 0.5549 | -0.1393| 0.3817 | 0.1014 | 0.715 |       |       |       |       |
| H17A   | 0.5488 | -0.2548| 0.3884 | 0.152  | 0.715 |       |       |       |       |
| H17B   | 0.5622 | -0.1213| 0.3330 | 0.152  | 0.715 |       |       |       |       |
| H17C   | 0.5887 | -0.1017| 0.4201 | 0.152  | 0.715 |       |       |       |       |
| C16A   | 0.4944 | -0.0438| 0.3548 | 0.0734 | 0.285 |       |       |       |       |
| H16A   | 0.4807 | -0.0976| 0.3946 | 0.088  | 0.285 |       |       |       |       |
| H16B   | 0.5442 | -0.1313| 0.3410 | 0.1014 | 0.285 |       |       |       |       |
| C17A   | 0.5325 | -0.2426| 0.3266 | 0.152  | 0.285 |       |       |       |       |
| H17B   | 0.5442 | -0.1313| 0.3410 | 0.1014 | 0.285 |       |       |       |       |
| H17C   | 0.5887 | -0.1017| 0.4201 | 0.152  | 0.285 |       |       |       |       |
| C16A   | 0.4944 | -0.0438| 0.3548 | 0.0734 | 0.285 |       |       |       |       |
| H16A   | 0.4807 | -0.0976| 0.3946 | 0.088  | 0.285 |       |       |       |       |
| H16B   | 0.5442 | -0.1313| 0.3410 | 0.1014 | 0.285 |       |       |       |       |
| C17A   | 0.5325 | -0.2426| 0.3266 | 0.152  | 0.285 |       |       |       |       |

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### Geometric parameters (Å, °)

| Bond/Distance            | Length/Angle         |
|--------------------------|----------------------|
| O1—C1                    | 1.2325 (16)          |
| O2—C9                    | 1.3722 (17)          |
| O2—C12                   | 1.413 (3)            |
| O3—C15                   | 1.1980 (17)          |
| O4—C15                   | 1.3243 (17)          |
| O4—C16A                  | 1.471 (3)            |
| O4—C16                   | 1.473 (2)            |
| N1—C4                    | 1.3030 (16)          |
| N1—N2                    | 1.3623 (15)          |
| N2—C1                    | 1.3773 (17)          |
| N2—C14                   | 1.4525 (16)          |
| C1—C2                    | 1.4347 (18)          |
| C2—C3                    | 1.3423 (17)          |
| C2—H2                    | 0.9300               |
| C3—C4                    | 1.4428 (16)          |
| C3—C5                    | 1.5131 (17)          |
| C4—C13                   | 1.4953 (17)          |
| C5—C6                    | 1.5027 (18)          |
| C5—H5A                   | 0.9700               |
| C5—H5B                   | 0.9700               |
| C6—C7                    | 1.3850 (19)          |
| C6—C11                   | 1.3894 (18)          |
| C7—C8                    | 1.384 (2)            |
| C7—H7                    | 0.9300               |
| C8—C9                    | 1.380 (2)            |
| C9—O2—C12                | 117.63 (16)          |
| C15—O4—C16A              | 114.3 (4)            |
| C15—O4—C16               | 116.62 (16)          |
| C4—N1—N2                 | 117.76 (10)          |
| N1—N2—C1                 | 125.72 (10)          |
| N1—N2—C14                | 116.08 (10)          |
| C1—N2—C14                | 118.20 (11)          |
| O1—C1—N2                 | 120.40 (12)          |
| O1—C1—C2                 | 125.62 (13)          |
| N2—C1—C2                 | 113.97 (11)          |
| C3—C2—C1                 | 122.19 (12)          |
| C3—O2—C12                | 118.9                |
| C1—C2—H2                 | 118.9                |
| C2—C3—C4                 | 117.55 (11)          |
| C2—C3—C5                 | 123.01 (11)          |
| C4—C3—C5                 | 119.44 (11)          |
| N1—C4—C3                 | 122.52 (11)          |
| N1—C4—C13                | 116.68 (11)          |
| C3—C4—C13                | 120.78 (11)          |
| Bond/Angle | Value 1 | Value 2 | Value 3 |
|------------|---------|---------|---------|
| C6—C5—C3  | 114.13  | (10)    |         |
| C6—C5—H5A | 108.7   |         |         |
| C6—C5—H5B | 108.7   |         |         |
| C3—C5—H5A | 108.7   |         |         |
| C3—C5—H5B | 108.7   |         |         |
| H5A—C5—H5B| 107.6   |         |         |
| C7—C6—C11 | 117.61  | (12)    |         |
| C7—C6—C5  | 121.46  | (12)    |         |
| C11—C6—C5 | 120.90  | (12)    |         |
| C8—C7—C6  | 122.08  | (13)    |         |
| C8—C7—H7  | 119.0   |         |         |
| C6—C7—H7  | 119.0   |         |         |
| C9—C8—C7  | 119.25  | (13)    |         |
| C9—C8—H8  | 120.4   |         |         |
| C7—C8—H8  | 120.4   |         |         |
| O2—C9—C8  | 124.76  | (14)    |         |
| O2—C9—C10 | 115.59  | (14)    |         |
| C8—C9—C10 | 119.63  | (13)    |         |
| C11—C10—C9| 120.36  | (13)    |         |
| C11—C10—H10| 119.8  |         |         |
| C9—C10—H10| 119.8   |         |         |
| C10—C11—C6| 121.05  | (13)    |         |
| C6—C11—H11| 119.5   |         |         |
| C6—C11—H11| 119.5   |         |         |
| O2—C12—H12A| 109.5  |         |         |
| C4—N1—N2—C1 | −3.99  | (18)    |         |
| C4—N1—N2—C14 | 176.09 | (11)    |         |
| N1—N2—C1—O1 | −175.15 | (13)   |         |
| C14—N2—C1—O1 | 4.8    | (2)     |         |
| N1—N2—C1—C2 | 6.4    | (2)     |         |
| C14—N2—C1—C2 | −173.70 | (12)   |         |
| O1—C1—C2—C3 | 177.80 | (15)    |         |
| N2—C1—C2—C3 | −3.8    | (2)     |         |
| C1—C2—C3—C4 | −0.6    | (2)     |         |
| C1—C2—C3—C5 | 178.73  | (13)    |         |
| N2—N1—C4—C3 | −1.25   | (17)    |         |
| N2—N1—C4—C13 | −179.54 | (11)   |         |
| C2—C3—C4—N1 | 3.40    | (18)    |         |
| C5—C3—C4—N1 | −175.96 | (11)   |         |
| C2—C3—C4—C13 | −178.39 | (12)   |         |
| C5—C3—C4—C13 | 2.25    | (18)    |         |
| C2—C3—C5—C6 | −9.45   | (19)    |         |
| C4—C3—C5—C6 | 169.88  | (11)    |         |
| C3—C5—C6—C7 | 90.46   | (16)    |         |
| C3—C5—C6—C11 | −87.41  | (15)   |         |
| C11—C6—C7—C8 | 1.3     | (2)     |         |
Hydrogen-bond geometry (Å, °)

*Cg1* is the centroid of the C1–C4/N1/N2 ring.

| D—H···A         | D—H | H···A | D···A   | D—H···A |
|-----------------|-----|-------|---------|---------|
| C14—H14B···O1i  | 0.97| 2.44  | 3.4041 (19) | 175     |
| C16—H16B···Cg1ii| 0.97| 2.86  | 3.586 (3)  | 132     |

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