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# 4-(2*H*-1,3-Benzodioxol-5-yl)-1-(4-methylphenyl)-1*H*-pyrazol-5-amine

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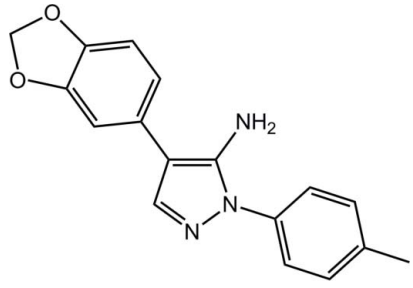
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.045; $wR$ factor = 0.136; data-to-parameter ratio = 16.1.

In the title compound, $C_{17}H_{15}N_3O_2$, two independent molecules (*A* and *B*) comprise the asymmetric unit. The major conformational difference arises in the relative orientation of the pyrazole ring amine and dioxole substituents which are *anti* in *A* and *syn* in *B*. The five-membered dioxole ring in each molecule has an envelope conformation with the methylene C atom as the flap. The mean plane through the benzodioxole and benzene groups make dihedral angles of 31.67 (8) and 68.22 (9)°, respectively, with the pyrazole ring in *A*; the equivalent values for *B* are 47.18 (7) and 49.08 (9)°. In the crystal, supramolecular zigzag chains along the *b*-axis direction arise as a result of N—H···N hydrogen bonding. These are consolidated into supramolecular double chains *via* C—H···O and C—H···$\pi$ interactions.

## Related literature

For background to the biological activity of amino substituted pyrazole derivatives, see: Tanitame *et al.* (2004); Chimenti *et al.* (2006); Ding *et al.* (2009); Shen *et al.* (2011); Deng *et al.* (2012). For a related structure, see: Muruganantham *et al.* (2007).




## Experimental

### Crystal data

$C_{17}H_{15}N_3O_2$
$M_r$ = 293.32
Triclinic, $P\overline{1}$
$a$ = 9.7690 (7) Å
$b$ = 10.4250 (7) Å
$c$ = 14.283 (1) Å
$\alpha$ = 96.626 (2)°
$\beta$ = 91.903 (2)°
$\gamma$ = 91.164 (2)°
$V$ = 1443.67 (17) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 K
0.40 × 0.25 × 0.20 mm

### Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min}$ = 0.965, $T_{max}$ = 0.982
29089 measured reflections
6620 independent reflections
4674 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.031

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.136
$S$ = 1.02
6620 reflections
412 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.19 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$

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

*Cg*1–*Cg*3 are the centroids of the C28–C33, C19–C24 and C2–C7 rings, respectviely.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N3—H1*N*···N5$^{i}$ | 0.89 (2) | 2.20 (2) | 3.059 (2) | 161 (2) |
| N6—H3*N*···N2$^{ii}$ | 0.89 (1) | 2.11 (1) | 2.9914 (19) | 170 (2) |
| C1—H1*C*···O3$^{ii}$ | 0.96 | 2.54 | 3.479 (2) | 164 |
| C3—H3···*Cg*1$^{iii}$ | 0.93 | 2.83 | 3.5365 (19) | 133 |
| C10—H10···*Cg*2$^{ii}$ | 0.93 | 2.88 | 3.6055 (17) | 135 |
| C27—H27···*Cg*3$^{i}$ | 0.93 | 2.94 | 3.5903 (18) | 128 |

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x+1, -y+1, -z+1$; (iii) $x+1, y, z+1$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2585).

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# supporting information

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## 4-(2*H*-1,3-Benzodioxol-5-yl)-1-(4-methylphenyl)-1*H*-pyrazol-5-amine

**Nilesh N. Gajera, Mukesh C. Patel, Mukesh M. Jotani and Edward R. T. Tiekink**

### S1. Comment

The amino substituted pyrazole unit is an important backbone in the area of synthetic as well as medicinal chemistry due to the broad range of biological activities of such compounds, such as anti-depressant, anti-anxiety, anti-fungal, anti-bacterial, anti-diabetic and anti-cancer (Tanitame *et al.*, 2004; Chimenti *et al.*, 2006; Ding *et al.*,2009; Shen *et al.*, 2011; Deng *et al.*, 2012). In this connection, the title compound, (I), was synthesized and its crystal structure is reported on herein.

Two independent molecules (A and B), comprise the asymmetric unit of (I), see Fig. 1. As seen from the overlay diagram, Fig. 2, different conformations are observed for both the benzodioxole and benzene substituents. The five-membered dioxole rings in each molecule has an envelope conformation with the methylene-C17 or C34 atoms being the flap atoms. The r.m.s. deviation of the five non-hydrogen atoms = 0.049 Å for the N1-containing molecule which is considerably less than 0.129 Å for the second independent molecule, where the C34 atom lies 0.115 (2) Å out of the mean plane. For the N1-containing molecule, with respect to the pyrazole ring (r.m.s. deviation = Å), the benzodioxole and benzene groups make dihedral angles of 31.67 (8) and 68.22 (9)°, respectively. The equivalent values for the N2-containing molecule are 47.18 (7)° and 49.08 (9)°, respectively. From a conformational point of view, the dioxole ring in the N1-containing molecule is *anti* to the amine substituent whereas it is *syn* for the second molecule. The observed conformations in (I) are similar to those in a closely related structure, *i.e.* diethyl 4-(benzo[*d*][1,3]dioxol-5-yl)-1*H*-pyrazol-3-yl-3-phosphonate (Muruganantham *et al.*, 2007).

The presence of N—H···N hydrogen bonding leads to supramolecular zigzag chains along the *b* axis in the crystal structure of (I), see Fig. 3 and Table 1. These are consolidated into supramolecular double chains *via* C—H···O and C—H···$\pi$ interactions (Table 1). These stack with no specific intermolecular interactions between them (Fig. 4).

### S2. Experimental

A mixture of 3,4-methyleneoxyphenyl acetonitrile (2 g, 0.012 mol) and *N*,*N*-dimethylformamide dimethylacetal (4.89 ml, 0.037 mol) was stirred at 355 K; progress of the reaction was monitored by TLC. At the end of the reaction, the solvent was removed under vacuum. The residual crude mass was mixed with 4-methyl phenyl hydrazine hydrochloride (1.96 g, 0.012 mol) in methanol (20 ml) at room temperature. The mixture was refluxed and the reaction progress was monitored by TLC. At the end of the reaction, the solvent was removed under reduced pressure. The residue was dissolved in water and $NaHCO_3$ solution was added until basic pH was obtained. The product was extracted in ethyl acetate (200 ml × 2), and this ethyl acetate layer passed through $Na_2SO_4$ and concentrated to dryness. The crude mass was purified by silica gel column chromatography, eluted with ethyl acetate:hexane (1:4) to produced 2.8 g of a yellow solid [Yield: 77%. *M*.pt: 422–423 K]. Single crystals suitable for X-ray measurements were obtained by repeated re-crystallization from ethyl acetate at room temperature.

## S3. Refinement

The C-bound H atoms were geometrically placed (C—H = 0.93–0.97 Å) and refined as riding with $U_{iso}$(H) = 1.2–1.5$U_{eq}$(C). The N-bound H-atom was refined with the distance restraint N—H = 0.89 (1) Å, and with $U_{iso}$(H) = 1.2$U_{eq}$(N). Being affected by the beam-stop, the (0 0 1) reflection was removed from the final cycles of refinement.

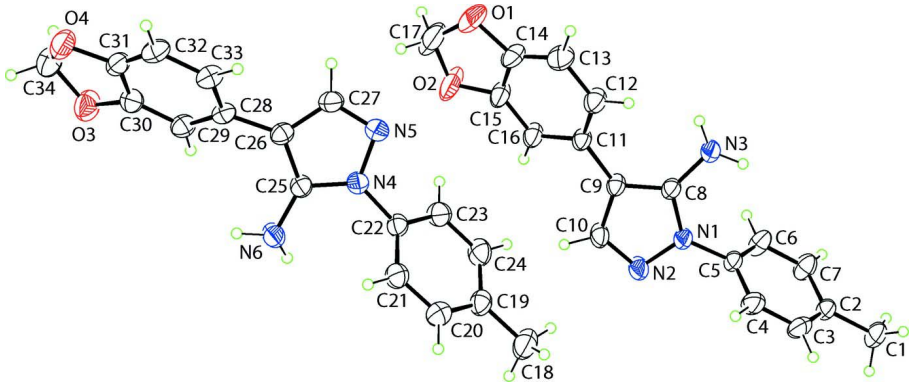


**Figure 1**

The molecular structure of the two independent molecules comprising the asymmetric unit of the title compound (I), showing the atom labelling. Displacement ellipsoids are drawn at the 35% probability level.

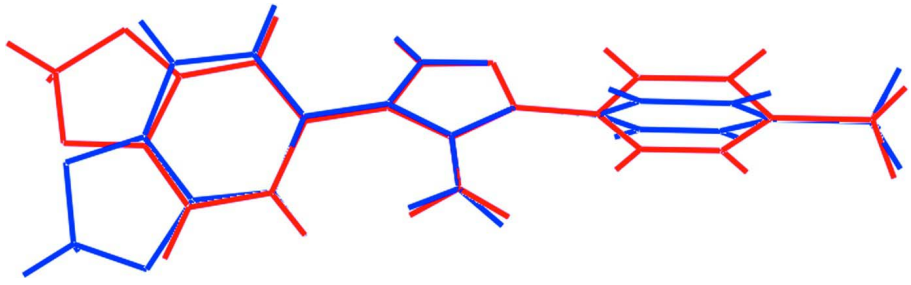

**Figure 2**

Overlay diagram of the N1- and inverted N2-containing molecules (red and blue, respectively), where the pyrazole rings have been superimposed.

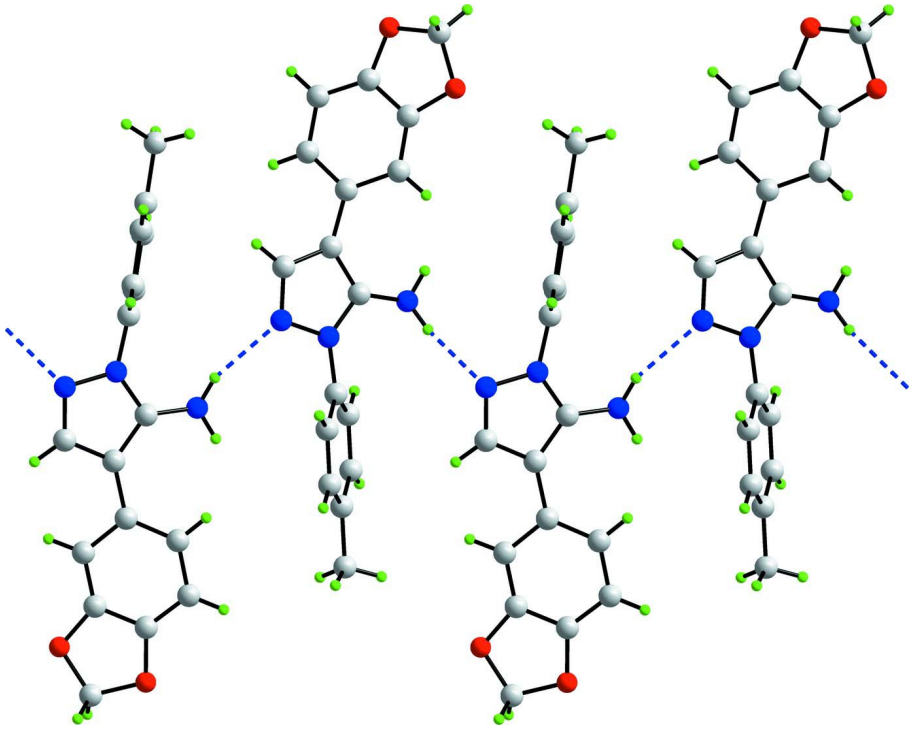

**Figure 3**

View of the supramolecular zigzag chain along the *b* axis in compound (I), mediated by N—H···N hydrogen bonds (dashed lines; see Table 1 for details).

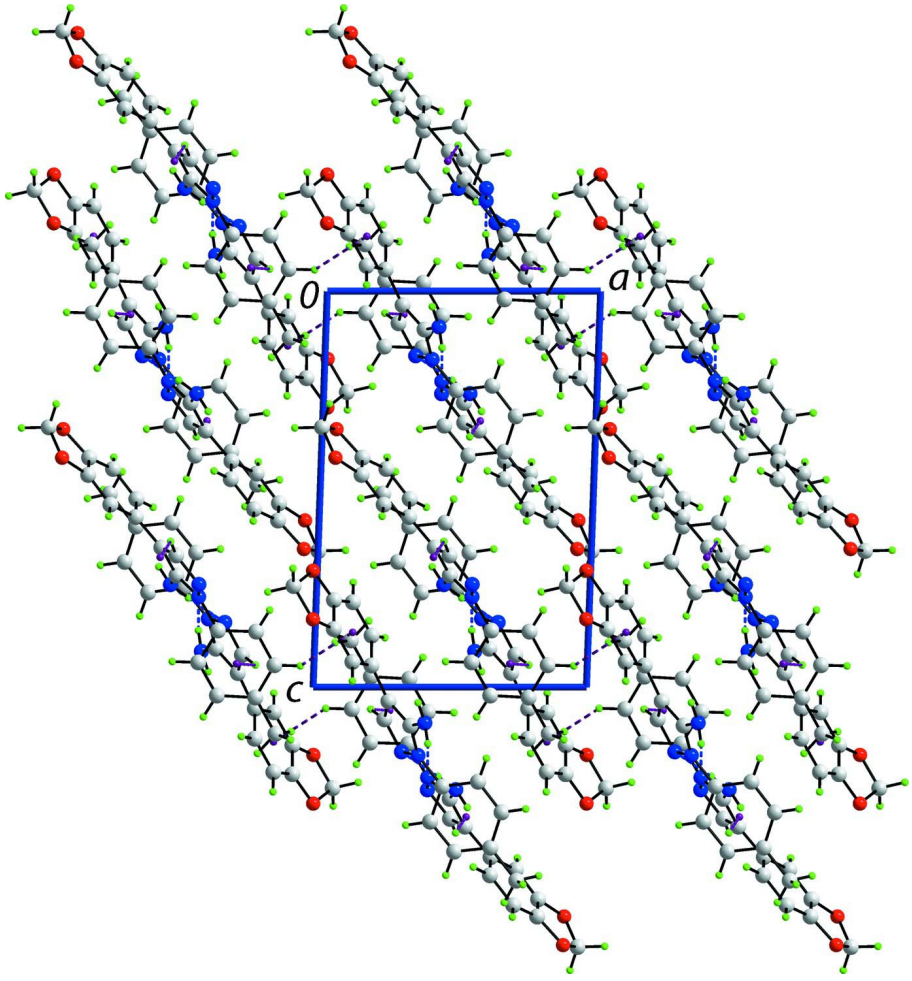


**Figure 4**

A view in projection along the *b* axis of the crystal packing of compound (I). The N—H···N, C—H···O (obscured) and C—H···$\pi$ interactions are shown as dashed lines (see Table 1 for details).

## 4-(2*H*-1,3-Benzodioxol-5-yl)-1-(4-methylphenyl)-1*H*-pyrazol-5-amine

*Crystal data*

$C_{17}H_{15}N_3O_2$
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Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a$ = 9.7690 (7) Å
$b$ = 10.4250 (7) Å
$c$ = 14.283 (1) Å
$\alpha$ = 96.626 (2)°
$\beta$ = 91.903 (2)°
$\gamma$ = 91.164 (2)°
$V$ = 1443.67 (17) Å$^3$
$Z$ = 4
$F(000)$ = 616
$D_x$ = 1.350 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71069 Å
Cell parameters from 5105 reflections
$\theta$ = 2.5–28.1°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 K
Block, light-brown
0.40 × 0.25 × 0.20 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.0 pixels mm$^{-1}$
$\omega$ and $\varphi$ scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min}$ = 0.965, $T_{max}$ = 0.982

29089 measured reflections
6620 independent reflections
4674 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.031
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 2.0°
$h$ = −12→12
$k$ = −13→13
$l$ = −17→18

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.136
$S$ = 1.02
6620 reflections
412 parameters
4 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
$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 0.2775P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.17 e Å$^{-3}$
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0100 (15)

*Special details*

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

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.05184 (17) | 0.01597 (17) | 0.34864 (10) | 0.0926 (5) |
| O2 | 0.05160 (17) | 0.22486 (16) | 0.42087 (11) | 0.0941 (5) |
| N1 | 0.56918 (13) | 0.17929 (11) | 0.77181 (8) | 0.0456 (3) |
| N2 | 0.56849 (16) | 0.29926 (12) | 0.74072 (9) | 0.0558 (4) |
| N3 | 0.46446 (17) | −0.02875 (14) | 0.74119 (11) | 0.0629 (4) |
| H1N | 0.5319 (15) | −0.0597 (18) | 0.7748 (12) | 0.075* |
| H2N | 0.4200 (19) | −0.0813 (16) | 0.6962 (11) | 0.075* |
| C1 | 0.8680 (2) | 0.1459 (2) | 1.11796 (13) | 0.0687 (5) |
| H1A | 0.9252 | 0.0718 | 1.1123 | 0.103* |
| H1B | 0.8048 | 0.1390 | 1.1673 | 0.103* |
| H1C | 0.9241 | 0.2228 | 1.1328 | 0.103* |
| C2 | 0.78997 (16) | 0.15254 (14) | 1.02637 (11) | 0.0478 (4) |
| C3 | 0.85553 (17) | 0.16857 (19) | 0.94457 (13) | 0.0624 (5) |
| H3 | 0.9506 | 0.1765 | 0.9464 | 0.075* |

| | | | | |
|---|---|---|---|---|
| C4 | 0.78454 (17) | 0.17326 (18) | 0.85982 (12) | 0.0583 (4) |
| H4 | 0.8314 | 0.1825 | 0.8053 | 0.070* |
| C5 | 0.64441 (15) | 0.16413 (13) | 0.85703 (10) | 0.0406 (3) |
| C6 | 0.57641 (16) | 0.14683 (18) | 0.93748 (11) | 0.0564 (4) |
| H6 | 0.4813 | 0.1391 | 0.9355 | 0.068* |
| C7 | 0.64917 (17) | 0.14102 (18) | 1.02109 (11) | 0.0575 (4) |
| H7 | 0.6022 | 0.1291 | 1.0751 | 0.069* |
| C8 | 0.48562 (15) | 0.09408 (13) | 0.71784 (10) | 0.0415 (3) |
| C9 | 0.42651 (15) | 0.15896 (13) | 0.64773 (9) | 0.0404 (3) |
| C10 | 0.48195 (18) | 0.28428 (15) | 0.66748 (10) | 0.0513 (4) |
| H10 | 0.4597 | 0.3509 | 0.6321 | 0.062* |
| C11 | 0.32854 (15) | 0.11204 (14) | 0.57068 (10) | 0.0420 (3) |
| C12 | 0.32865 (19) | −0.01296 (16) | 0.52498 (12) | 0.0569 (4) |
| H12 | 0.3908 | −0.0707 | 0.5458 | 0.068* |
| C13 | 0.2395 (2) | −0.05524 (18) | 0.44922 (13) | 0.0680 (5) |
| H13 | 0.2408 | −0.1394 | 0.4195 | 0.082* |
| C14 | 0.15023 (19) | 0.03216 (19) | 0.42066 (12) | 0.0610 (5) |
| C15 | 0.14910 (18) | 0.15617 (18) | 0.46424 (12) | 0.0578 (4) |
| C16 | 0.23427 (17) | 0.19885 (15) | 0.53917 (11) | 0.0509 (4) |
| H16 | 0.2301 | 0.2830 | 0.5686 | 0.061* |
| C17 | −0.0015 (3) | 0.1391 (3) | 0.34386 (19) | 0.1104 (9) |
| H17A | −0.1007 | 0.1344 | 0.3455 | 0.132* |
| H17B | 0.0230 | 0.1703 | 0.2851 | 0.132* |
| O3 | −0.00982 (14) | 0.54440 (13) | −0.17121 (10) | 0.0746 (4) |
| O4 | −0.01550 (13) | 0.38075 (14) | −0.29402 (9) | 0.0685 (4) |
| N4 | 0.39249 (13) | 0.31673 (12) | 0.17245 (9) | 0.0458 (3) |
| N5 | 0.33173 (15) | 0.19573 (12) | 0.16344 (10) | 0.0563 (4) |
| N6 | 0.41337 (19) | 0.50194 (14) | 0.09039 (10) | 0.0634 (4) |
| H3N | 0.427 (2) | 0.5557 (16) | 0.1430 (9) | 0.076* |
| H4N | 0.386 (2) | 0.5369 (18) | 0.0393 (10) | 0.076* |
| C18 | 0.7688 (2) | 0.4236 (2) | 0.48865 (14) | 0.0753 (6) |
| H18A | 0.7271 | 0.3984 | 0.5438 | 0.113* |
| H18B | 0.7928 | 0.5140 | 0.4987 | 0.113* |
| H18C | 0.8498 | 0.3747 | 0.4765 | 0.113* |
| C19 | 0.66949 (18) | 0.39817 (15) | 0.40553 (12) | 0.0525 (4) |
| C20 | 0.70590 (18) | 0.42017 (18) | 0.31628 (13) | 0.0586 (4) |
| H20 | 0.7938 | 0.4516 | 0.3077 | 0.070* |
| C21 | 0.61593 (17) | 0.39708 (17) | 0.23905 (12) | 0.0534 (4) |
| H21 | 0.6435 | 0.4125 | 0.1796 | 0.064* |
| C22 | 0.48521 (16) | 0.35108 (14) | 0.25076 (10) | 0.0430 (3) |
| C23 | 0.44556 (18) | 0.32943 (17) | 0.33975 (11) | 0.0539 (4) |
| H23 | 0.3571 | 0.2995 | 0.3486 | 0.065* |
| C24 | 0.5377 (2) | 0.35237 (17) | 0.41535 (11) | 0.0587 (4) |
| H24 | 0.5103 | 0.3365 | 0.4748 | 0.070* |
| C25 | 0.36066 (16) | 0.38099 (14) | 0.09701 (10) | 0.0418 (3) |
| C26 | 0.27733 (15) | 0.29921 (14) | 0.03560 (10) | 0.0427 (3) |
| C27 | 0.26475 (17) | 0.18800 (15) | 0.08121 (12) | 0.0532 (4) |
| H27 | 0.2137 | 0.1152 | 0.0558 | 0.064* |

| | | | | |
|---|---|---|---|---|
| C28 | 0.21039 (14) | 0.32219 (14) | −0.05457 (10) | 0.0424 (3) |
| C29 | 0.14039 (16) | 0.43657 (15) | −0.06373 (11) | 0.0480 (4) |
| H29 | 0.1429 | 0.5044 | −0.0153 | 0.058* |
| C30 | 0.06824 (16) | 0.44450 (15) | −0.14665 (12) | 0.0500 (4) |
| C31 | 0.06488 (15) | 0.34652 (17) | −0.21981 (11) | 0.0487 (4) |
| C32 | 0.13435 (16) | 0.23582 (17) | −0.21447 (11) | 0.0524 (4) |
| H32 | 0.1332 | 0.1702 | −0.2645 | 0.063* |
| C33 | 0.20731 (15) | 0.22566 (15) | −0.13039 (11) | 0.0484 (4) |
| H33 | 0.2561 | 0.1511 | −0.1247 | 0.058* |
| C34 | −0.0848 (2) | 0.4919 (2) | −0.25516 (15) | 0.0751 (6) |
| H34A | −0.1776 | 0.4686 | −0.2404 | 0.090* |
| H34B | −0.0891 | 0.5551 | −0.2999 | 0.090* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.1014 (11) | 0.1036 (12) | 0.0658 (9) | −0.0138 (9) | −0.0459 (8) | −0.0029 (8) |
| O2 | 0.1030 (11) | 0.0994 (11) | 0.0758 (10) | 0.0264 (9) | −0.0522 (9) | 0.0041 (8) |
| N1 | 0.0574 (8) | 0.0396 (6) | 0.0388 (7) | −0.0019 (5) | −0.0142 (6) | 0.0058 (5) |
| N2 | 0.0851 (10) | 0.0404 (7) | 0.0410 (7) | −0.0072 (6) | −0.0169 (7) | 0.0076 (5) |
| N3 | 0.0804 (11) | 0.0434 (7) | 0.0639 (10) | −0.0094 (7) | −0.0347 (8) | 0.0143 (6) |
| C1 | 0.0753 (13) | 0.0721 (12) | 0.0569 (11) | −0.0031 (10) | −0.0314 (9) | 0.0100 (9) |
| C2 | 0.0530 (9) | 0.0442 (8) | 0.0448 (8) | −0.0021 (7) | −0.0169 (7) | 0.0045 (6) |
| C3 | 0.0398 (9) | 0.0831 (12) | 0.0649 (11) | −0.0149 (8) | −0.0139 (8) | 0.0191 (9) |
| C4 | 0.0478 (9) | 0.0790 (12) | 0.0498 (9) | −0.0143 (8) | −0.0029 (7) | 0.0188 (8) |
| C5 | 0.0467 (8) | 0.0388 (7) | 0.0352 (7) | −0.0006 (6) | −0.0108 (6) | 0.0034 (6) |
| C6 | 0.0380 (8) | 0.0868 (12) | 0.0438 (9) | 0.0081 (8) | −0.0041 (7) | 0.0053 (8) |
| C7 | 0.0527 (10) | 0.0838 (12) | 0.0359 (8) | 0.0059 (9) | −0.0010 (7) | 0.0060 (8) |
| C8 | 0.0457 (8) | 0.0405 (7) | 0.0374 (7) | 0.0016 (6) | −0.0081 (6) | 0.0029 (6) |
| C9 | 0.0477 (8) | 0.0417 (7) | 0.0314 (7) | 0.0060 (6) | −0.0039 (6) | 0.0027 (6) |
| C10 | 0.0778 (11) | 0.0413 (8) | 0.0344 (8) | 0.0026 (7) | −0.0111 (7) | 0.0064 (6) |
| C11 | 0.0487 (8) | 0.0456 (8) | 0.0312 (7) | 0.0033 (6) | −0.0052 (6) | 0.0036 (6) |
| C12 | 0.0684 (11) | 0.0495 (9) | 0.0505 (9) | 0.0083 (8) | −0.0148 (8) | −0.0011 (7) |
| C13 | 0.0876 (14) | 0.0545 (10) | 0.0567 (11) | −0.0033 (9) | −0.0176 (10) | −0.0094 (8) |
| C14 | 0.0654 (11) | 0.0727 (12) | 0.0416 (9) | −0.0104 (9) | −0.0182 (8) | 0.0011 (8) |
| C15 | 0.0610 (10) | 0.0688 (11) | 0.0435 (9) | 0.0069 (8) | −0.0157 (8) | 0.0106 (8) |
| C16 | 0.0639 (10) | 0.0485 (8) | 0.0391 (8) | 0.0091 (7) | −0.0119 (7) | 0.0018 (6) |
| C17 | 0.119 (2) | 0.117 (2) | 0.0897 (18) | 0.0012 (17) | −0.0649 (16) | 0.0106 (15) |
| O3 | 0.0836 (9) | 0.0649 (8) | 0.0748 (9) | 0.0165 (7) | −0.0190 (7) | 0.0105 (6) |
| O4 | 0.0636 (8) | 0.0895 (10) | 0.0523 (7) | 0.0004 (7) | −0.0138 (6) | 0.0123 (6) |
| N4 | 0.0543 (8) | 0.0406 (6) | 0.0420 (7) | −0.0039 (6) | −0.0040 (6) | 0.0051 (5) |
| N5 | 0.0611 (9) | 0.0426 (7) | 0.0653 (9) | −0.0088 (6) | −0.0129 (7) | 0.0122 (6) |
| N6 | 0.1031 (12) | 0.0469 (8) | 0.0389 (8) | −0.0208 (8) | −0.0140 (8) | 0.0076 (6) |
| C18 | 0.0871 (14) | 0.0711 (12) | 0.0653 (12) | 0.0104 (10) | −0.0261 (11) | 0.0042 (10) |
| C19 | 0.0632 (11) | 0.0436 (8) | 0.0494 (9) | 0.0081 (7) | −0.0097 (8) | 0.0023 (7) |
| C20 | 0.0499 (9) | 0.0651 (11) | 0.0609 (11) | −0.0029 (8) | −0.0042 (8) | 0.0102 (8) |
| C21 | 0.0544 (10) | 0.0629 (10) | 0.0440 (9) | −0.0031 (8) | 0.0029 (7) | 0.0109 (7) |
| C22 | 0.0523 (9) | 0.0383 (7) | 0.0379 (8) | 0.0025 (6) | −0.0025 (6) | 0.0028 (6) |

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|---|---|---|---|---|---|---|
| C23 | 0.0564 (10) | 0.0600 (10) | 0.0450 (9) | −0.0057 (8) | 0.0047 (7) | 0.0055 (7) |
| C24 | 0.0777 (12) | 0.0623 (10) | 0.0360 (8) | 0.0017 (9) | 0.0020 (8) | 0.0058 (7) |
| C25 | 0.0510 (8) | 0.0396 (7) | 0.0340 (7) | 0.0004 (6) | 0.0014 (6) | 0.0005 (6) |
| C26 | 0.0402 (8) | 0.0420 (8) | 0.0440 (8) | 0.0027 (6) | −0.0014 (6) | −0.0018 (6) |
| C27 | 0.0508 (9) | 0.0422 (8) | 0.0648 (11) | −0.0065 (7) | −0.0122 (8) | 0.0041 (7) |
| C28 | 0.0353 (7) | 0.0480 (8) | 0.0425 (8) | −0.0029 (6) | 0.0001 (6) | 0.0000 (6) |
| C29 | 0.0497 (9) | 0.0464 (8) | 0.0459 (8) | 0.0007 (7) | −0.0007 (7) | −0.0025 (6) |
| C30 | 0.0478 (9) | 0.0492 (9) | 0.0535 (9) | 0.0018 (7) | −0.0012 (7) | 0.0088 (7) |
| C31 | 0.0394 (8) | 0.0666 (10) | 0.0399 (8) | −0.0067 (7) | −0.0023 (6) | 0.0070 (7) |
| C32 | 0.0455 (9) | 0.0631 (10) | 0.0444 (9) | −0.0042 (7) | 0.0002 (7) | −0.0098 (7) |
| C33 | 0.0403 (8) | 0.0503 (9) | 0.0517 (9) | 0.0030 (6) | −0.0020 (7) | −0.0061 (7) |
| C34 | 0.0674 (12) | 0.0865 (14) | 0.0729 (13) | 0.0056 (11) | −0.0168 (10) | 0.0199 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C14 | 1.378 (2) | O3—C30 | 1.3741 (19) |
| O1—C17 | 1.403 (3) | O3—C34 | 1.431 (2) |
| O2—C15 | 1.376 (2) | O4—C31 | 1.3824 (19) |
| O2—C17 | 1.413 (3) | O4—C34 | 1.421 (3) |
| N1—C8 | 1.3492 (18) | N4—C25 | 1.3635 (18) |
| N1—N2 | 1.3746 (17) | N4—N5 | 1.3737 (18) |
| N1—C5 | 1.4270 (17) | N4—C22 | 1.4237 (19) |
| N2—C10 | 1.3159 (19) | N5—C27 | 1.319 (2) |
| N3—C8 | 1.373 (2) | N6—C25 | 1.367 (2) |
| N3—H1N | 0.890 (9) | N6—H3N | 0.889 (9) |
| N3—H2N | 0.891 (9) | N6—H4N | 0.888 (9) |
| C1—C2 | 1.501 (2) | C18—C19 | 1.504 (2) |
| C1—H1A | 0.9600 | C18—H18A | 0.9600 |
| C1—H1B | 0.9600 | C18—H18B | 0.9600 |
| C1—H1C | 0.9600 | C18—H18C | 0.9600 |
| C2—C3 | 1.376 (2) | C19—C20 | 1.378 (2) |
| C2—C7 | 1.377 (2) | C19—C24 | 1.381 (3) |
| C3—C4 | 1.381 (2) | C20—C21 | 1.383 (2) |
| C3—H3 | 0.9300 | C20—H20 | 0.9300 |
| C4—C5 | 1.369 (2) | C21—C22 | 1.377 (2) |
| C4—H4 | 0.9300 | C21—H21 | 0.9300 |
| C5—C6 | 1.374 (2) | C22—C23 | 1.383 (2) |
| C6—C7 | 1.377 (2) | C23—C24 | 1.379 (2) |
| C6—H6 | 0.9300 | C23—H23 | 0.9300 |
| C7—H7 | 0.9300 | C24—H24 | 0.9300 |
| C8—C9 | 1.3884 (19) | C25—C26 | 1.382 (2) |
| C9—C10 | 1.398 (2) | C26—C27 | 1.399 (2) |
| C9—C11 | 1.4674 (19) | C26—C28 | 1.472 (2) |
| C10—H10 | 0.9300 | C27—H27 | 0.9300 |
| C11—C12 | 1.389 (2) | C28—C33 | 1.390 (2) |
| C11—C16 | 1.404 (2) | C28—C29 | 1.403 (2) |
| C12—C13 | 1.391 (2) | C29—C30 | 1.370 (2) |
| C12—H12 | 0.9300 | C29—H29 | 0.9300 |

| | | | |
|---|---|---|---|
| C13—C14 | 1.361 (3) | C30—C31 | 1.374 (2) |
| C13—H13 | 0.9300 | C31—C32 | 1.359 (2) |
| C14—C15 | 1.369 (3) | C32—C33 | 1.392 (2) |
| C15—C16 | 1.361 (2) | C32—H32 | 0.9300 |
| C16—H16 | 0.9300 | C33—H33 | 0.9300 |
| C17—H17A | 0.9700 | C34—H34A | 0.9700 |
| C17—H17B | 0.9700 | C34—H34B | 0.9700 |
| | | | |
| C14—O1—C17 | 105.27 (16) | C30—O3—C34 | 104.72 (14) |
| C15—O2—C17 | 105.11 (17) | C31—O4—C34 | 104.44 (13) |
| C8—N1—N2 | 111.81 (12) | C25—N4—N5 | 111.66 (12) |
| C8—N1—C5 | 129.50 (12) | C25—N4—C22 | 130.28 (12) |
| N2—N1—C5 | 118.45 (12) | N5—N4—C22 | 117.78 (12) |
| C10—N2—N1 | 103.64 (12) | C27—N5—N4 | 103.58 (12) |
| C8—N3—H1N | 115.8 (13) | C25—N6—H3N | 118.6 (13) |
| C8—N3—H2N | 113.6 (13) | C25—N6—H4N | 115.1 (13) |
| H1N—N3—H2N | 119.2 (19) | H3N—N6—H4N | 116.5 (19) |
| C2—C1—H1A | 109.5 | C19—C18—H18A | 109.5 |
| C2—C1—H1B | 109.5 | C19—C18—H18B | 109.5 |
| H1A—C1—H1B | 109.5 | H18A—C18—H18B | 109.5 |
| C2—C1—H1C | 109.5 | C19—C18—H18C | 109.5 |
| H1A—C1—H1C | 109.5 | H18A—C18—H18C | 109.5 |
| H1B—C1—H1C | 109.5 | H18B—C18—H18C | 109.5 |
| C3—C2—C7 | 117.43 (14) | C20—C19—C24 | 117.10 (15) |
| C3—C2—C1 | 121.71 (15) | C20—C19—C18 | 121.41 (17) |
| C7—C2—C1 | 120.86 (16) | C24—C19—C18 | 121.49 (16) |
| C2—C3—C4 | 122.06 (15) | C19—C20—C21 | 122.14 (17) |
| C2—C3—H3 | 119.0 | C19—C20—H20 | 118.9 |
| C4—C3—H3 | 119.0 | C21—C20—H20 | 118.9 |
| C5—C4—C3 | 119.24 (16) | C22—C21—C20 | 119.58 (15) |
| C5—C4—H4 | 120.4 | C22—C21—H21 | 120.2 |
| C3—C4—H4 | 120.4 | C20—C21—H21 | 120.2 |
| C4—C5—C6 | 119.89 (14) | C21—C22—C23 | 119.46 (15) |
| C4—C5—N1 | 119.88 (14) | C21—C22—N4 | 121.55 (13) |
| C6—C5—N1 | 120.15 (13) | C23—C22—N4 | 118.85 (14) |
| C5—C6—C7 | 119.95 (15) | C24—C23—C22 | 119.72 (16) |
| C5—C6—H6 | 120.0 | C24—C23—H23 | 120.1 |
| C7—C6—H6 | 120.0 | C22—C23—H23 | 120.1 |
| C2—C7—C6 | 121.39 (15) | C23—C24—C19 | 121.99 (15) |
| C2—C7—H7 | 119.3 | C23—C24—H24 | 119.0 |
| C6—C7—H7 | 119.3 | C19—C24—H24 | 119.0 |
| N1—C8—N3 | 120.78 (13) | N4—C25—N6 | 121.33 (13) |
| N1—C8—C9 | 107.35 (12) | N4—C25—C26 | 107.16 (13) |
| N3—C8—C9 | 131.66 (14) | N6—C25—C26 | 131.45 (14) |
| C8—C9—C10 | 103.36 (12) | C25—C26—C27 | 103.66 (13) |
| C8—C9—C11 | 129.93 (13) | C25—C26—C28 | 129.50 (14) |
| C10—C9—C11 | 126.70 (13) | C27—C26—C28 | 126.78 (14) |
| N2—C10—C9 | 113.82 (13) | N5—C27—C26 | 113.94 (14) |

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|---|---|---|---|
| N2—C10—H10 | 123.1 | N5—C27—H27 | 123.0 |
| C9—C10—H10 | 123.1 | C26—C27—H27 | 123.0 |
| C12—C11—C16 | 118.51 (14) | C33—C28—C29 | 118.87 (14) |
| C12—C11—C9 | 122.89 (13) | C33—C28—C26 | 119.78 (13) |
| C16—C11—C9 | 118.54 (13) | C29—C28—C26 | 121.19 (13) |
| C11—C12—C13 | 122.64 (15) | C30—C29—C28 | 117.52 (14) |
| C11—C12—H12 | 118.7 | C30—C29—H29 | 121.2 |
| C13—C12—H12 | 118.7 | C28—C29—H29 | 121.2 |
| C14—C13—C12 | 116.94 (16) | C29—C30—C31 | 122.34 (15) |
| C14—C13—H13 | 121.5 | C29—C30—O3 | 128.16 (15) |
| C12—C13—H13 | 121.5 | C31—C30—O3 | 109.50 (14) |
| C13—C14—C15 | 121.39 (15) | C32—C31—C30 | 121.80 (15) |
| C13—C14—O1 | 128.86 (17) | C32—C31—O4 | 128.42 (15) |
| C15—C14—O1 | 109.75 (16) | C30—C31—O4 | 109.78 (15) |
| C16—C15—C14 | 122.54 (15) | C31—C32—C33 | 116.63 (14) |
| C16—C15—O2 | 127.73 (17) | C31—C32—H32 | 121.7 |
| C14—C15—O2 | 109.74 (15) | C33—C32—H32 | 121.7 |
| C15—C16—C11 | 117.97 (15) | C28—C33—C32 | 122.80 (15) |
| C15—C16—H16 | 121.0 | C28—C33—H33 | 118.6 |
| C11—C16—H16 | 121.0 | C32—C33—H33 | 118.6 |
| O1—C17—O2 | 109.53 (17) | O4—C34—O3 | 107.51 (14) |
| O1—C17—H17A | 109.8 | O4—C34—H34A | 110.2 |
| O2—C17—H17A | 109.8 | O3—C34—H34A | 110.2 |
| O1—C17—H17B | 109.8 | O4—C34—H34B | 110.2 |
| O2—C17—H17B | 109.8 | O3—C34—H34B | 110.2 |
| H17A—C17—H17B | 108.2 | H34A—C34—H34B | 108.5 |

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|---|---|---|---|
| C8—N1—N2—C10 | 0.48 (18) | C25—N4—N5—C27 | 0.77 (18) |
| C5—N1—N2—C10 | −174.38 (13) | C22—N4—N5—C27 | −173.75 (13) |
| C7—C2—C3—C4 | 0.1 (3) | C24—C19—C20—C21 | −0.4 (3) |
| C1—C2—C3—C4 | 179.25 (17) | C18—C19—C20—C21 | 179.89 (16) |
| C2—C3—C4—C5 | 1.2 (3) | C19—C20—C21—C22 | 0.3 (3) |
| C3—C4—C5—C6 | −1.8 (3) | C20—C21—C22—C23 | 0.4 (2) |
| C3—C4—C5—N1 | 174.93 (15) | C20—C21—C22—N4 | −175.21 (14) |
| C8—N1—C5—C4 | 117.59 (19) | C25—N4—C22—C21 | −46.4 (2) |
| N2—N1—C5—C4 | −68.6 (2) | N5—N4—C22—C21 | 126.91 (16) |
| C8—N1—C5—C6 | −65.7 (2) | C25—N4—C22—C23 | 137.94 (17) |
| N2—N1—C5—C6 | 108.15 (18) | N5—N4—C22—C23 | −48.74 (19) |
| C4—C5—C6—C7 | 1.2 (3) | C21—C22—C23—C24 | −0.9 (2) |
| N1—C5—C6—C7 | −175.60 (15) | N4—C22—C23—C24 | 174.84 (14) |
| C3—C2—C7—C6 | −0.8 (3) | C22—C23—C24—C19 | 0.7 (3) |
| C1—C2—C7—C6 | −179.96 (17) | C20—C19—C24—C23 | −0.1 (3) |
| C5—C6—C7—C2 | 0.2 (3) | C18—C19—C24—C23 | 179.61 (16) |
| N2—N1—C8—N3 | −175.36 (15) | N5—N4—C25—N6 | −178.24 (15) |
| C5—N1—C8—N3 | −1.2 (2) | C22—N4—C25—N6 | −4.6 (2) |
| N2—N1—C8—C9 | 0.06 (18) | N5—N4—C25—C26 | −0.68 (17) |
| C5—N1—C8—C9 | 174.19 (14) | C22—N4—C25—C26 | 172.97 (14) |
| N1—C8—C9—C10 | −0.53 (17) | N4—C25—C26—C27 | 0.29 (16) |

| | | | |
|---|---|---|---|
| N3—C8—C9—C10 | 174.19 (18) | N6—C25—C26—C27 | 177.51 (18) |
| N1—C8—C9—C11 | 179.89 (14) | N4—C25—C26—C28 | 177.61 (14) |
| N3—C8—C9—C11 | −5.4 (3) | N6—C25—C26—C28 | −5.2 (3) |
| N1—N2—C10—C9 | −0.85 (19) | N4—N5—C27—C26 | −0.59 (19) |
| C8—C9—C10—N2 | 0.89 (19) | C25—C26—C27—N5 | 0.20 (19) |
| C11—C9—C10—N2 | −179.51 (14) | C28—C26—C27—N5 | −177.22 (14) |
| C8—C9—C11—C12 | −34.1 (2) | C25—C26—C28—C33 | 138.92 (16) |
| C10—C9—C11—C12 | 146.40 (18) | C27—C26—C28—C33 | −44.3 (2) |
| C8—C9—C11—C16 | 148.63 (16) | C25—C26—C28—C29 | −45.8 (2) |
| C10—C9—C11—C16 | −30.9 (2) | C27—C26—C28—C29 | 130.89 (17) |
| C16—C11—C12—C13 | 0.2 (3) | C33—C28—C29—C30 | 2.3 (2) |
| C9—C11—C12—C13 | −177.07 (17) | C26—C28—C29—C30 | −172.96 (14) |
| C11—C12—C13—C14 | 0.1 (3) | C28—C29—C30—C31 | −1.2 (2) |
| C12—C13—C14—C15 | 0.4 (3) | C28—C29—C30—O3 | 178.57 (16) |
| C12—C13—C14—O1 | −179.75 (19) | C34—O3—C30—C29 | −167.77 (18) |
| C17—O1—C14—C13 | −174.4 (2) | C34—O3—C30—C31 | 11.99 (19) |
| C17—O1—C14—C15 | 5.4 (2) | C29—C30—C31—C32 | −0.6 (3) |
| C13—C14—C15—C16 | −1.3 (3) | O3—C30—C31—C32 | 179.63 (15) |
| O1—C14—C15—C16 | 178.84 (17) | C29—C30—C31—O4 | 179.92 (15) |
| C13—C14—C15—O2 | 178.86 (19) | O3—C30—C31—O4 | 0.15 (19) |
| O1—C14—C15—O2 | −1.0 (2) | C34—O4—C31—C32 | 168.27 (18) |
| C17—O2—C15—C16 | 176.4 (2) | C34—O4—C31—C30 | −12.29 (19) |
| C17—O2—C15—C14 | −3.8 (3) | C30—C31—C32—C33 | 1.1 (2) |
| C14—C15—C16—C11 | 1.6 (3) | O4—C31—C32—C33 | −179.54 (15) |
| O2—C15—C16—C11 | −178.62 (18) | C29—C28—C33—C32 | −1.9 (2) |
| C12—C11—C16—C15 | −1.0 (2) | C26—C28—C33—C32 | 173.45 (14) |
| C9—C11—C16—C15 | 176.39 (15) | C31—C32—C33—C28 | 0.2 (2) |
| C14—O1—C17—O2 | −7.8 (3) | C31—O4—C34—O3 | 19.6 (2) |
| C15—O2—C17—O1 | 7.2 (3) | C30—O3—C34—O4 | −19.6 (2) |

*Hydrogen-bond geometry (Å, º)*

Cg1–Cg3 are the centroids of the C28–C33, C19–C24 and C2–C7 rings, respectviely.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H1*N*···N5$^{i}$ | 0.89 (2) | 2.20 (2) | 3.059 (2) | 161 (2) |
| N6—H3*N*···N2$^{ii}$ | 0.89 (1) | 2.11 (1) | 2.9914 (19) | 170 (2) |
| C1—H1*C*···O3$^{ii}$ | 0.96 | 2.54 | 3.479 (2) | 164 |
| C3—H3···*Cg*1$^{iii}$ | 0.93 | 2.83 | 3.5365 (19) | 133 |
| C10—H10···*Cg*2$^{ii}$ | 0.93 | 2.88 | 3.6055 (17) | 135 |
| C27—H27···*Cg*3$^{i}$ | 0.93 | 2.94 | 3.5903 (18) | 128 |

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