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# A monoclinic polymorph of 4-(2*H*-1,3-benzodioxol-5-yl)-1-(4-methylphenyl)-1*H*-pyrazol-5-amine

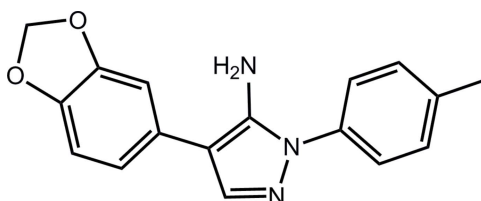
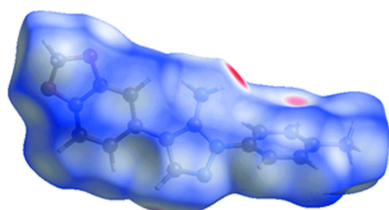
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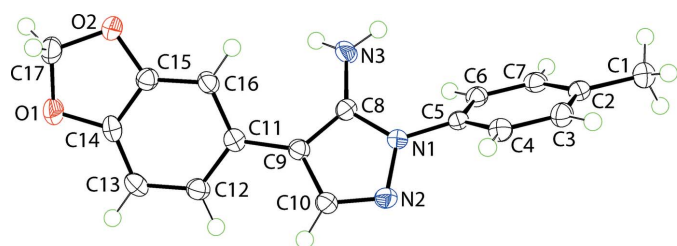
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The title compound, C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>, is a monoclinic polymorph (*P*2<sub>1</sub>/*c* with *Z*' = 1) of the previously reported triclinic (*P* $\bar{1}$  with *Z*' = 2) form [Gajera *et al.* (2013). *Acta Cryst. E* **69**, o736–o737]. The molecule in the monoclinic polymorph features a central pyrazolyl ring with an N-bound *p*-tolyl group and a C-bound 1,3-benzodioxolyl fused-ring system on either side of the C atom bearing the amino group. The dihedral angles between the central ring and the N- and C-bound rings are 50.06 (5) and 27.27 (5)°, respectively. The angle between the pendent rings is 77.31 (4)°, indicating the molecule has a twisted conformation. The five-membered dioxolyl ring has an envelope conformation with the methylene C atom being the flap. The relative disposition of the amino and dioxolyl substituents is *syn*. One of the independent molecules in the triclinic form has a similar *syn* disposition but the other has an *anti* arrangement of these substituents. In the crystal structure of the monoclinic form, molecules assemble into supramolecular helical chains *via* amino–pyrazolyl N–H···N hydrogen bonds. These are linked into layers *via* C–H··· $\pi$  interactions, and layers stack along the *a* axis with no specific interactions between them.

## 1. Chemical context

It is the broad range of biological activities, such as anti-depressant, anti-anxiety, anti-fungal, anti-bacterial, anti-diabetic, anti-cancer, *etc.* (Tanitame *et al.*, 2004; Chimenti *et al.*, 2006; Ding *et al.*, 2009; Shen *et al.*, 2011; Deng *et al.*, 2012), that continues to inspire interest in compounds containing the amino-substituted pyrazole unit. It was in this context that the crystal structure of 4-(2*H*-1,3-benzodioxol-5-yl)-1-(4-methylphenyl)-1*H*-pyrazol-5-amine (I) was originally determined (Gajera *et al.*, 2013). Subsequently, during scale up, crystals of the monoclinic form were isolated from recrystallization of (I) from ethyl acetate, the same solvent system that afforded the original triclinic polymorph. Herein, the crystal and molecular structures of the monoclinic form of (I), hereafter (mI), are described and compared with the triclinic polymorph, (tI).





**Figure 1**  
The molecular structure of the molecule found in the monoclinic polymorph showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

## 2. Structural commentary

The molecule in (mI), Fig. 1, comprises a central and almost planar pyrazolyl ring (r.m.s. deviation of the five atoms = 0.0043 Å) flanked by an N-bound *p*-tolyl group and a C-bound 1,3-benzodioxolyl fused ring system. In the latter, the five-membered dioxolyl ring adopts an envelope conformation with the methylene-C17 atom being the flap; the C17 atom lies 0.318 (2) Å out of the least-squares plane defined by the O1, O2, C14 and C15 atoms (r.m.s. deviation = 0.0005 Å). The dihedral angles between the central ring and the N- and C-bound six-membered rings are 50.06 (5) and 27.27 (5)°, respectively. The dihedral angle between the six-membered rings is 77.31 (4)°, indicating an overall twisted arrangement. In general terms, the relative disposition of the amino and dioxolyl substituents may be described as being *syn*.

While (mI) crystallizes with  $Z' = 1$ , the triclinic polymorph, (tI), crystallizes with  $Z' = 2$  (Gajera *et al.*, 2013). In the latter, the molecules have quite different conformations. In one of the independent molecules, the amino and dioxolyl substituents are *syn*, as for (mI), and in the other these substituents are *anti*. These differences in molecular conformations are highlighted in Fig. 2. The *syn/anti* distinction is quite clear from this overlap diagram where the dioxolyl ring obviously occupies a different position in the second independent mol-

**Table 1**  
Dihedral angle (°) data for the three independent molecules in (mI) and (tI).

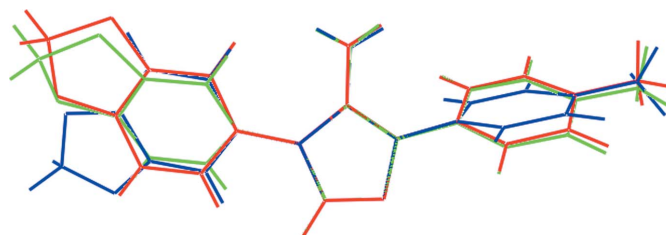
Structure	pyrazolyl/ <i>p</i> -tolyl	pyrazolyl/benzo-C <sub>6</sub>	<i>p</i> -tolyl/benzo-C <sub>6</sub>
(mI)	50.06 (5)	27.27 (5)	77.31 (4)
(tI), molecule <i>a</i>	49.08 (9)	47.18 (7)	85.22 (8)
(tI), molecule <i>b</i>	68.22 (9)	31.67 (8)	80.63 (8)

**Table 2**  
Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids of the C2–C7 and C11–C16 rings, respectively.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N3–H1N...N2 <sup>i</sup>	0.88 (2)	2.16 (2)	2.9981 (16)	159 (1)
C10–H10...Cg1 <sup>ii</sup>	0.95	2.97	3.6753 (14)	133
C17–H17B...Cg2 <sup>iii</sup>	0.99	2.66	3.6334 (15)	169

Symmetry codes: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $x, -y + \frac{1}{2}, z - \frac{3}{2}$ .

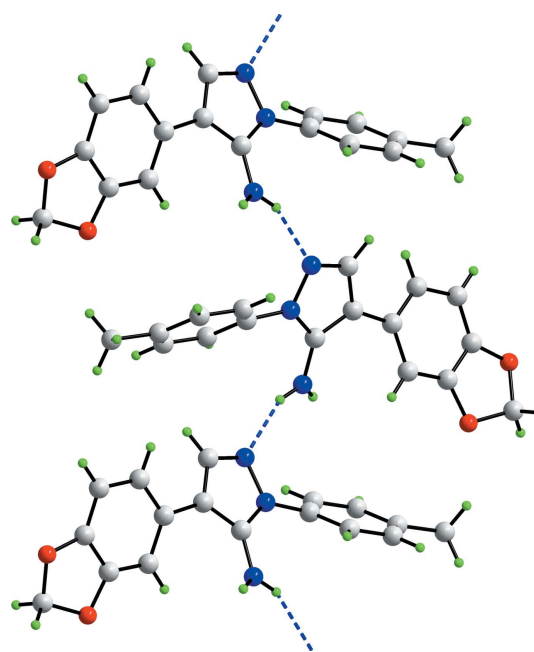


**Figure 2**  
Overlay diagram of the title compound, (mI), red image, with the two independent molecules in (tI), green (molecule *a*) and blue (*b*) images. The molecules have been overlapped so that the central pyrazolyl rings are coincident.

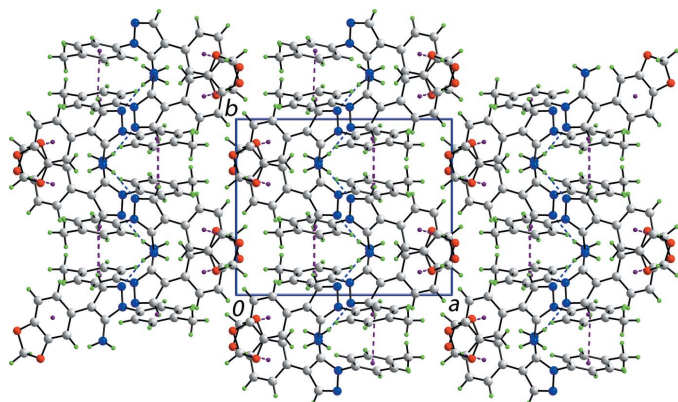
ecule of (tI, blue image). Also evident from Fig. 2 are variations in the relative dispositions of six-membered rings. These variations are quantified in Table 1.

## 3. PXRD study

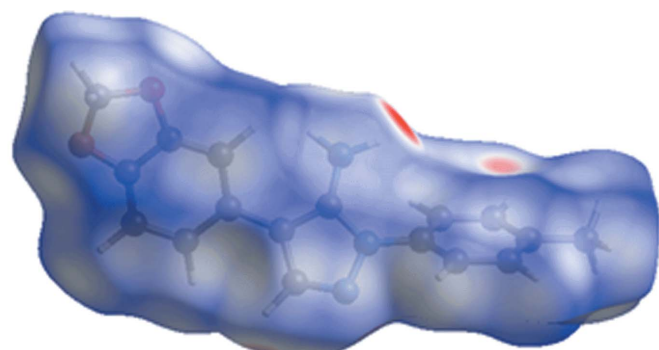
In order to ascertain the nature of the crystalline residue isolated from recrystallization of (I) from ethyl acetate solution, a powder X-ray diffraction (PXRD) experiment was performed on a PANalytical Empyrean XRD system with Cu K $\alpha$ 1 radiation ( $\lambda = 1.54056$  Å) in the  $2\theta$  range of 5 to 50° with a step size of 0.026°. The pattern was analyzed with *X'Pert HighScore Plus* (PANalytical, 2009). This analysis indicated that the ratio of (mI) to (tI) in the overall sample was 49.1:50.9. This distribution suggests that effectively in the sample there is a 3:1 ratio of molecules with a *syn* disposition of the amino and dioxolyl substituents to those with a *trans* arrangement.



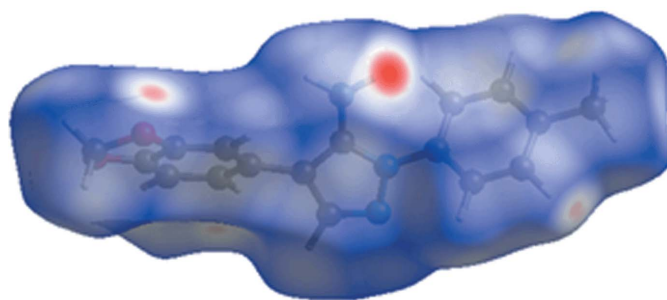
**Figure 3**  
A view of a supramolecular helical chain aligned along the *b* axis and mediated by amino–pyrazolyl N–H...N hydrogen bonds shown as blue dashed lines.



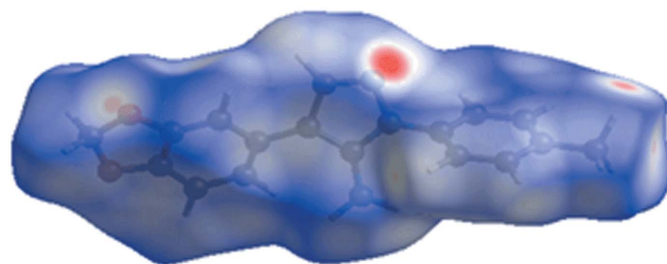
**Figure 4**  
Unit-cell contents shown in projection down the  $c$  axis. The  $N-H\cdots N$  and  $C-H\cdots\pi$  interactions are shown as blue and purple dashed lines, respectively.



(a)



(b)



(c)

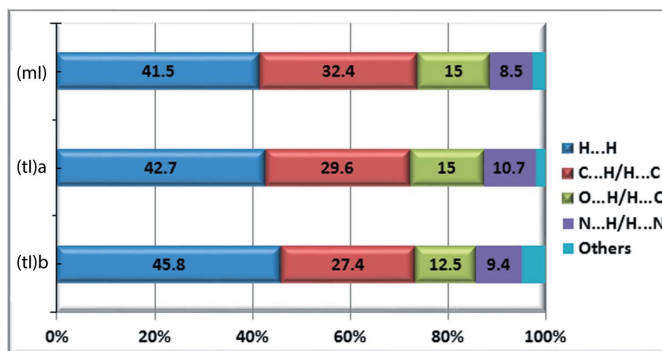
**Figure 5**  
Views of the Hirshfeld surfaces for (a) (mI), (b) (tI) – molecule  $a$ , and (c) (tI) – molecule  $b$ .

#### 4. Supramolecular features

The most notable feature of the crystal packing in (mI) is the formation of supramolecular helical chains aligned along the  $b$  axis and mediated by amino-pyrazolyl  $N-H\cdots N$  hydrogen bonds, Fig. 3 and Table 2. The chains are consolidated into layers in the  $bc$  plane by pyrazolyl-tolyl  $C10-H\cdots\pi$  and methylene-benzo- $C_6$   $C17-H\cdots\pi$  interactions, Table 2. The layers inter-digitate along the  $a$  axis whereby the dioxolyl rings face each other, Fig. 4. The  $C-H\cdots O$  interactions are at distances beyond the standard criteria (Spek, 2009). In the packing scheme just described, no specific role is found for the second amino- $H_2N$  atom. To a first approximation, the mode of association between molecules in (tI) is similar in that supramolecular chains are formed. These comprise alternating independent molecules  $a$  and  $b$  that are connected by amino-pyrazolyl  $N-H\cdots N$  hydrogen bonds. The difference is that in (tI), the chains have a zigzag topology. Chains in (tI) are connected by  $C-H\cdots O$  and  $C-H\cdots\pi$  interactions.

#### 5. Analysis of the Hirshfeld surfaces

In order to investigate further the nature of the crystal packing in (mI) and (tI), an analysis of the Hirshfeld surfaces (Spackman & Jayatilaka, 2009) was undertaken employing *CrystalExplorer* (Wolff *et al.*, 2012). The Hirshfeld surfaces were mapped over  $d_{\text{norm}}$  for each of the three molecules, Fig. 5. The points of contact corresponding to the amino-pyrazolyl  $N-H\cdots N$  hydrogen bonds are recognized easily by deep-red depressions on the Hirshfeld surfaces of all three molecules. The  $C-H\cdots\pi$  interactions in (mI) are indicated by both diminutive spots and light-red regions on the surface. These are also apparent in (tI) with additional features arising from the  $C-H\cdots O$  contacts, Fig. 5. The fingerprint plots (Rohl *et al.*, 2008) were also calculated and enabled a delineation of the relative contribution of the different intermolecular contacts to the respective crystal structures. These contributions are illustrated graphically in Fig. 6. Despite the different modes of association between the respective molecules, to a first approximation the relative contributions to the surfaces are similar.



**Figure 6**  
Relative contributions of various intermolecular contacts to the Hirshfeld surface area in (a) mI, and of (tI) molecules (b)  $a$  and (c)  $b$ .

**Table 3**  
Experimental details.

Crystal data	
Chemical formula	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>
<i>M</i> <sub>r</sub>	293.32
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	13.9652 (3), 10.6898 (2), 9.8459 (2)
β (°)	109.844 (2)
<i>V</i> (Å <sup>3</sup> )	1382.57 (5)
<i>Z</i>	4
Radiation type	Cu Kα
μ (mm <sup>-1</sup> )	0.77
Crystal size (mm)	0.35 × 0.25 × 0.15
Data collection	
Diffractometer	Agilent SuperNova Dual diffractometer with an Atlas detector
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Agilent, 2014)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.989, 1.000
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	4379, 2582, 2289
<i>R</i> <sub>int</sub>	0.013
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.609
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.036, 0.096, 1.03
No. of reflections	2582
No. of parameters	206
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.19, -0.27

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SHELXL97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

## 6. Database survey

A search of the Cambridge Structural Database (Groom & Allen, 2014), revealed there are no direct analogues of (I), *i.e.* 1,3-N- and C-disubstituted species. There are four examples of 1,3,4 trisubstituted analogues (Abu Thaher *et al.*, 2012; and references therein).

## 7. Synthesis and crystallization

The title compound was synthesized according to the same synthetic process as described in the original report (Gajera *et al.*, 2013). Single crystals suitable for X-ray measurements in the form of light-brown prisms were obtained from its ethyl acetate solution at room temperature.

## 8. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Carbon-bound H-atoms were placed in calculated positions (C–H = 0.95–0.99 Å) and were

included in the refinement in the riding model approximation, with *U*<sub>iso</sub>(H) set to 1.2–1.5*U*<sub>eq</sub>(C). The N-bound H atoms were located in a difference Fourier map but were refined with a distance restraint of N–H = 0.88 ± 0.01 Å, and with *U*<sub>iso</sub>(H) set to 1.2*U*<sub>eq</sub>(N).

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## supporting information

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## A monoclinic polymorph of 4-(2*H*-1,3-benzodioxol-5-yl)-1-(4-methylphenyl)-1*H*-pyrazol-5-amine

Mukesh M. Jotani, Nilesh N. Gajera, Mukesh C. Patel, Herman H. Y. Sung and Edward R. T. Tiekink

### Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: *SHELXL97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); 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).

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

#### Crystal data

$C_{17}H_{15}N_3O_2$	$F(000) = 616$
$M_r = 293.32$	$D_x = 1.409 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 13.9652 (3) \text{ \AA}$	Cell parameters from 2900 reflections
$b = 10.6898 (2) \text{ \AA}$	$\theta = 5.3\text{--}75.6^\circ$
$c = 9.8459 (2) \text{ \AA}$	$\mu = 0.77 \text{ mm}^{-1}$
$\beta = 109.844 (2)^\circ$	$T = 100 \text{ K}$
$V = 1382.57 (5) \text{ \AA}^3$	Prism, light-brown
$Z = 4$	$0.35 \times 0.25 \times 0.15 \text{ mm}$

#### Data collection

Agilent SuperNova Dual	4379 measured reflections
diffractometer with an Atlas detector	2582 independent reflections
Radiation source: SuperNova (Cu) X-ray	2289 reflections with $I > 2\sigma(I)$
Source	$R_{\text{int}} = 0.013$
Mirror monochromator	$\theta_{\text{max}} = 70.0^\circ$ , $\theta_{\text{min}} = 5.3^\circ$
$\omega$ scans	$h = -16 \rightarrow 12$
Absorption correction: multi-scan	$k = -12 \rightarrow 12$
( <i>CrysAlis PRO</i> ; Agilent, 2014)	$l = -11 \rightarrow 11$
$T_{\text{min}} = 0.989$ , $T_{\text{max}} = 1.000$	

#### Refinement

Refinement on $F^2$	206 parameters
Least-squares matrix: full	2 restraints
$R[F^2 > 2\sigma(F^2)] = 0.036$	Hydrogen site location: mixed
$wR(F^2) = 0.096$	H atoms treated by a mixture of independent
$S = 1.03$	and constrained refinement
2582 reflections	

$$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.5203P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$$

*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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	-0.01538 (7)	0.79537 (9)	0.05812 (10)	0.0229 (2)
O2	0.09248 (7)	0.63677 (9)	0.17958 (10)	0.0229 (2)
N1	0.47346 (8)	0.93081 (10)	0.71284 (11)	0.0146 (2)
N2	0.46867 (8)	1.04737 (10)	0.65038 (11)	0.0168 (2)
N3	0.38155 (8)	0.73744 (11)	0.67648 (13)	0.0229 (3)
H1N	0.4302 (10)	0.6978 (15)	0.7442 (15)	0.028*
H2N	0.3203 (8)	0.7054 (15)	0.6459 (17)	0.028*
C1	0.79815 (10)	0.85389 (13)	1.24901 (15)	0.0226 (3)
H1A	0.7964	0.9221	1.3147	0.034*
H1B	0.8637	0.8547	1.2330	0.034*
H1C	0.7896	0.7737	1.2917	0.034*
C2	0.71312 (10)	0.87116 (12)	1.10672 (14)	0.0178 (3)
C3	0.73229 (9)	0.91569 (12)	0.98529 (14)	0.0188 (3)
H3	0.8002	0.9347	0.9919	0.023*
C4	0.65366 (9)	0.93269 (12)	0.85479 (14)	0.0173 (3)
H4	0.6679	0.9627	0.7728	0.021*
C5	0.55400 (9)	0.90549 (11)	0.84473 (13)	0.0146 (3)
C6	0.53312 (9)	0.86113 (11)	0.96412 (13)	0.0161 (3)
H6	0.4651	0.8427	0.9574	0.019*
C7	0.61276 (10)	0.84398 (12)	1.09371 (14)	0.0174 (3)
H7	0.5984	0.8130	1.1752	0.021*
C8	0.39184 (9)	0.85823 (12)	0.63961 (13)	0.0149 (3)
C9	0.33011 (9)	0.93033 (12)	0.52569 (13)	0.0154 (3)
C10	0.38242 (10)	1.04516 (12)	0.54044 (13)	0.0170 (3)
H10	0.3579	1.1141	0.4773	0.020*
C11	0.23592 (9)	0.89631 (12)	0.40828 (13)	0.0157 (3)
C12	0.16893 (9)	0.99103 (12)	0.33479 (14)	0.0180 (3)
H12	0.1828	1.0747	0.3683	0.022*
C13	0.08223 (10)	0.96750 (13)	0.21382 (14)	0.0199 (3)
H13	0.0379	1.0328	0.1646	0.024*
C14	0.06491 (9)	0.84515 (13)	0.17031 (13)	0.0177 (3)
C15	0.12917 (9)	0.75009 (12)	0.24281 (14)	0.0170 (3)
C16	0.21486 (9)	0.77116 (12)	0.36133 (14)	0.0169 (3)
H16	0.2580	0.7044	0.4095	0.020*
C17	0.01608 (10)	0.66946 (14)	0.04489 (14)	0.0217 (3)
H17A	-0.0427	0.6118	0.0237	0.026*

H17B            0.0442            0.6637            -0.0347            0.026\*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0172 (4)	0.0250 (5)	0.0207 (5)	0.0016 (4)	-0.0013 (4)	-0.0017 (4)
O2	0.0204 (5)	0.0185 (5)	0.0223 (5)	-0.0015 (4)	-0.0023 (4)	-0.0026 (4)
N1	0.0150 (5)	0.0125 (5)	0.0151 (5)	-0.0002 (4)	0.0036 (4)	0.0007 (4)
N2	0.0198 (5)	0.0137 (5)	0.0161 (5)	-0.0013 (4)	0.0050 (4)	0.0010 (4)
N3	0.0144 (5)	0.0165 (6)	0.0307 (7)	-0.0019 (4)	-0.0017 (5)	0.0071 (5)
C1	0.0221 (7)	0.0219 (7)	0.0195 (7)	-0.0008 (5)	0.0015 (5)	0.0003 (5)
C2	0.0197 (6)	0.0134 (6)	0.0178 (6)	0.0013 (5)	0.0030 (5)	-0.0025 (5)
C3	0.0148 (6)	0.0188 (6)	0.0217 (7)	-0.0007 (5)	0.0046 (5)	-0.0014 (5)
C4	0.0183 (6)	0.0170 (6)	0.0171 (6)	0.0000 (5)	0.0066 (5)	-0.0001 (5)
C5	0.0158 (6)	0.0116 (6)	0.0147 (6)	0.0013 (4)	0.0031 (5)	-0.0023 (5)
C6	0.0153 (6)	0.0142 (6)	0.0189 (6)	0.0003 (5)	0.0061 (5)	-0.0016 (5)
C7	0.0223 (6)	0.0141 (6)	0.0162 (6)	0.0009 (5)	0.0071 (5)	-0.0008 (5)
C8	0.0127 (6)	0.0154 (6)	0.0171 (6)	-0.0001 (4)	0.0057 (5)	-0.0013 (5)
C9	0.0153 (6)	0.0147 (6)	0.0160 (6)	0.0009 (5)	0.0052 (5)	0.0005 (5)
C10	0.0199 (6)	0.0150 (6)	0.0149 (6)	0.0002 (5)	0.0046 (5)	0.0014 (5)
C11	0.0141 (6)	0.0182 (6)	0.0157 (6)	-0.0001 (5)	0.0062 (5)	0.0017 (5)
C12	0.0179 (6)	0.0157 (6)	0.0202 (6)	0.0011 (5)	0.0063 (5)	0.0011 (5)
C13	0.0178 (6)	0.0198 (7)	0.0204 (7)	0.0045 (5)	0.0045 (5)	0.0046 (5)
C14	0.0132 (6)	0.0238 (7)	0.0143 (6)	0.0002 (5)	0.0026 (5)	0.0015 (5)
C15	0.0160 (6)	0.0166 (6)	0.0183 (6)	-0.0010 (5)	0.0057 (5)	-0.0003 (5)
C16	0.0141 (6)	0.0171 (6)	0.0181 (6)	0.0016 (5)	0.0035 (5)	0.0025 (5)
C17	0.0180 (6)	0.0242 (7)	0.0190 (6)	-0.0007 (5)	0.0013 (5)	-0.0026 (5)

*Geometric parameters (Å, °)*

O2—C15	1.3787 (16)	C4—H4	0.9500
O2—C17	1.4347 (15)	C5—C6	1.3872 (18)
O1—C14	1.3856 (15)	C6—C7	1.3911 (17)
O1—C17	1.4354 (17)	C6—H6	0.9500
N1—C8	1.3649 (16)	C7—H7	0.9500
N1—N2	1.3810 (15)	C8—C9	1.3925 (17)
N1—C5	1.4258 (15)	C9—C10	1.4105 (17)
N2—C10	1.3183 (16)	C9—C11	1.4719 (17)
N3—C8	1.3621 (17)	C10—H10	0.9500
N3—H1N	0.883 (9)	C11—C12	1.4016 (18)
N3—H2N	0.875 (9)	C11—C16	1.4134 (18)
C1—C2	1.5091 (17)	C12—C13	1.4032 (17)
C1—H1A	0.9800	C12—H12	0.9500
C1—H1B	0.9800	C13—C14	1.372 (2)
C1—H1C	0.9800	C13—H13	0.9500
C2—C7	1.3940 (19)	C14—C15	1.3830 (18)
C2—C3	1.3946 (19)	C15—C16	1.3771 (17)
C3—C4	1.3898 (17)	C16—H16	0.9500

C3—H3	0.9500	C17—H17A	0.9900
C4—C5	1.3921 (18)	C17—H17B	0.9900
C15—O2—C17	104.43 (10)	N3—C8—N1	122.88 (11)
C14—O1—C17	104.05 (9)	N3—C8—C9	130.31 (12)
C8—N1—N2	111.85 (10)	N1—C8—C9	106.77 (11)
C8—N1—C5	129.22 (11)	C8—C9—C10	103.96 (11)
N2—N1—C5	118.74 (10)	C8—C9—C11	129.77 (12)
C10—N2—N1	104.01 (10)	C10—C9—C11	126.12 (11)
C8—N3—H1N	122.2 (11)	N2—C10—C9	113.40 (11)
C8—N3—H2N	117.3 (11)	N2—C10—H10	123.3
H1N—N3—H2N	119.0 (16)	C9—C10—H10	123.3
C2—C1—H1A	109.5	C12—C11—C16	119.12 (12)
C2—C1—H1B	109.5	C12—C11—C9	119.26 (12)
H1A—C1—H1B	109.5	C16—C11—C9	121.47 (11)
C2—C1—H1C	109.5	C11—C12—C13	122.76 (12)
H1A—C1—H1C	109.5	C11—C12—H12	118.6
H1B—C1—H1C	109.5	C13—C12—H12	118.6
C7—C2—C3	118.16 (12)	C14—C13—C12	116.48 (12)
C7—C2—C1	120.64 (12)	C14—C13—H13	121.8
C3—C2—C1	121.20 (12)	C12—C13—H13	121.8
C4—C3—C2	121.06 (12)	C13—C14—C15	121.64 (12)
C4—C3—H3	119.5	C13—C14—O1	128.63 (12)
C2—C3—H3	119.5	C15—C14—O1	109.69 (12)
C3—C4—C5	119.71 (12)	C16—C15—O2	127.53 (12)
C3—C4—H4	120.1	C16—C15—C14	122.83 (12)
C5—C4—H4	120.1	O2—C15—C14	109.63 (11)
C6—C5—C4	120.25 (11)	C15—C16—C11	117.16 (11)
C6—C5—N1	120.59 (11)	C15—C16—H16	121.4
C4—C5—N1	119.06 (11)	C11—C16—H16	121.4
C5—C6—C7	119.32 (11)	O2—C17—O1	107.40 (10)
C5—C6—H6	120.3	O2—C17—H17A	110.2
C7—C6—H6	120.3	O1—C17—H17A	110.2
C6—C7—C2	121.51 (12)	O2—C17—H17B	110.2
C6—C7—H7	119.2	O1—C17—H17B	110.2
C2—C7—H7	119.2	H17A—C17—H17B	108.5
C8—N1—N2—C10	1.15 (13)	C8—C9—C10—N2	0.51 (14)
C5—N1—N2—C10	-174.21 (10)	C11—C9—C10—N2	-175.48 (11)
C7—C2—C3—C4	0.04 (19)	C8—C9—C11—C12	158.82 (13)
C1—C2—C3—C4	-179.34 (12)	C10—C9—C11—C12	-26.24 (19)
C2—C3—C4—C5	0.3 (2)	C8—C9—C11—C16	-25.6 (2)
C3—C4—C5—C6	-0.26 (19)	C10—C9—C11—C16	149.34 (13)
C3—C4—C5—N1	176.08 (11)	C16—C11—C12—C13	-1.36 (19)
C8—N1—C5—C6	-47.97 (18)	C9—C11—C12—C13	174.33 (11)
N2—N1—C5—C6	126.47 (12)	C11—C12—C13—C14	0.57 (19)
C8—N1—C5—C4	135.70 (13)	C12—C13—C14—C15	0.53 (19)
N2—N1—C5—C4	-49.86 (16)	C12—C13—C14—O1	178.07 (12)



C4—C5—C6—C7	-0.10 (18)	C17—O1—C14—C13	168.94 (14)
N1—C5—C6—C7	-176.39 (11)	C17—O1—C14—C15	-13.28 (14)
C5—C6—C7—C2	0.44 (19)	C17—O2—C15—C16	-168.01 (13)
C3—C2—C7—C6	-0.41 (19)	C17—O2—C15—C14	13.12 (14)
C1—C2—C7—C6	178.98 (12)	C13—C14—C15—C16	-0.8 (2)
N2—N1—C8—N3	177.01 (11)	O1—C14—C15—C16	-178.81 (11)
C5—N1—C8—N3	-8.2 (2)	C13—C14—C15—O2	178.09 (12)
N2—N1—C8—C9	-0.87 (14)	O1—C14—C15—O2	0.12 (15)
C5—N1—C8—C9	173.88 (11)	O2—C15—C16—C11	-178.70 (12)
N3—C8—C9—C10	-177.44 (13)	C14—C15—C16—C11	0.03 (19)
N1—C8—C9—C10	0.23 (13)	C12—C11—C16—C15	1.02 (18)
N3—C8—C9—C11	-1.7 (2)	C9—C11—C16—C15	-174.57 (11)
N1—C8—C9—C11	176.01 (12)	C15—O2—C17—O1	-21.31 (13)
N1—N2—C10—C9	-1.00 (14)	C14—O1—C17—O2	21.29 (13)

*Hydrogen-bond geometry (Å, °)*

Cg1 and Cg2 are the centroids of the C2—C7 and C11—C16 rings, respectively.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H1 <i>N</i> ...N2 <sup>i</sup>	0.88 (2)	2.16 (2)	2.9981 (16)	159 (1)
C10—H10...Cg1 <sup>ii</sup>	0.95	2.97	3.6753 (14)	133
C17—H17 <i>B</i> ...Cg2 <sup>iii</sup>	0.99	2.66	3.6334 (15)	169

Symmetry codes: (i)  $-x+1, y-1/2, -z+3/2$ ; (ii)  $-x+1, y+1/2, -z+3/2$ ; (iii)  $x, -y+1/2, z-3/2$ .