

N'-(*Z*)-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)methylidene]-2-hydroxybenzohydrazide

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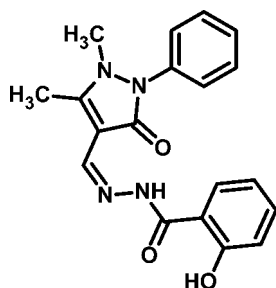
Received 23 December 2011; accepted 5 January 2012

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.043; wR factor = 0.119; data-to-parameter ratio = 17.2.

In the title compound, $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_3$, the pyrazole ring is oriented at dihedral angles of 41.12 (7) and 12.25 (10)°, respectively, with respect to the planes of the phenyl and benzene rings. Intramolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds generate seven- and six-membered $S(7)$ and $S(6)$ ring motifs, respectively.

Related literature

For the biological activity of Schiff bases, see: Lau *et al.* (1999); More *et al.* (2002); Safwat *et al.* (1988); Sharma *et al.* (1998); Pandeya *et al.* (1999). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_3$
 $M_r = 350.37$
 Monoclinic, $C2/c$
 $a = 25.2357$ (6) Å

$b = 8.5624$ (2) Å
 $c = 16.0329$ (4) Å
 $\beta = 104.048$ (1)°
 $V = 3360.75$ (14) Å³

$Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹

$T = 296$ K
 $0.22 \times 0.06 \times 0.05$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2007)
 $T_{\min} = 0.980$, $T_{\max} = 0.995$

16063 measured reflections
 4174 independent reflections
 2653 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.119$
 $S = 1.02$
 4174 reflections
 243 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.16$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3O}\cdots\text{O2}$	0.95 (2)	1.62 (2)	2.5076 (17)	155 (2)
$\text{N4}-\text{H4N}\cdots\text{O1}$	0.978 (18)	1.763 (18)	2.7140 (16)	163.3 (16)

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); 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, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: WinGX (Farrugia, 1999) and PLATON.

MA expresses his gratitude to the Pakistan Council of Scientific and Industrial Research Laboratories Complex, Karachi, the Department of Chemistry, University of Karachi, and the Department of Chemistry, Govt. College University Lahore, for providing financial support, research facilities and X-ray diffraction facilities, respectively.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5039).

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Acta Cryst. (2012). E68, o352 [doi:10.1107/S1600536812000402]

N'-(*Z*)-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl)methylidene]-2-hydroxybenzohydrazide

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Comment

The Schiff base ligands have importance for elucidating the mechanism of racemization and transamination reactions in biological systems (Lau *et al.*, 1999) and exhibit remarkable biological activities such as antibacterial (More *et al.*, 2002), antifungal (Safwat *et al.*, 1988), anticancer (Sharma *et al.*, 1998) and anti HIV activities (Pandeya *et al.*, 1999). Such applications lead us to report the synthesis and characterization of Schiff base ligand, *N'*-((1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl) methylene)-2-hydroxybenzohydrazide.

In the crystal structure of title compound, two nitrogen and three carbon atoms of pyrazole ring are sp^2 hybridized, whose ring shows an r.m.s. deviation of about 0.1 Å with the maximum deviation of from N1 [0.1256 (12) Å] and C8 [0.1237 (10) Å]. The molecule contains N—H and O—H groups but no classical intermolecular hydrogen bonding has been observed. Only intramolecular hydrogen bonding produces six-membered *S*(6) and seven-membered *S*(7) (Bernstein *et al.*, 1995) ring motifs through O—H \cdots O and N—H \cdots O interactions (Table 1 and Fig. 1). The two ring motifs O1/C7/C8/C10/N3/N4/H4N and O2/C11/C12/C13/O3/H3O are inclined at a dihedral angle of 3.46 (4)°. The phenyl ring (C1—C6) is twisted at 41.12 (7) and 41.64 (7)°, respectively, with the pyrazole ring and *o*-hydroxy benzoyl ring (C12—C17).

Experimental

1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1*H*-pyrazole-4-carbaldehyde (1 mol) and 2-hydroxybenzohydrazide (1 mol) were added in 50 ml ethanol and add 3–4 drops of conc. H₂SO₄. The mixture was refluxed with stirring for 5 h at 70 °C on water bath. The reaction mixture was kept at room temperature overnight and white crystals were obtained. These were filtered, washed with cooled methanol, dried and recrystallized from methanol.

Refinement

C-bound H atoms were positioned with idealized geometry with C—H = 0.93 Å for aromatic and C—H = 0.96 Å for methyl group, and were refined using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic or $1.5U_{\text{eq}}(\text{C})$ for methyl carbon atoms. The N and O-bound H atoms were located in a difference Fourier map and the positional parameters were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$; the refined distances are N—H = 0.978 (18) Å and O—H = 0.95 (2) Å

Figures

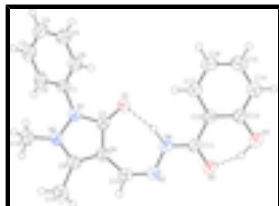


Fig. 1. The molecular structure of the title compound, with 50% displacement ellipsoids. The hydrogen bonds are shown with dashed lines.

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Crystal data

$C_{19}H_{18}N_4O_3$

$M_r = 350.37$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 25.2357\ (6)\ \text{\AA}$

$b = 8.5624\ (2)\ \text{\AA}$

$c = 16.0329\ (4)\ \text{\AA}$

$\beta = 104.048\ (1)^\circ$

$V = 3360.75\ (14)\ \text{\AA}^3$

$Z = 8$

$F(000) = 1472$

$D_x = 1.385\ \text{Mg m}^{-3}$

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

Cell parameters from 3642 reflections

$\theta = 2.5\text{--}25.1^\circ$

$\mu = 0.10\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Needle, colorless

$0.22 \times 0.06 \times 0.05\ \text{mm}$

Data collection

Bruker Kappa APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2007)

$T_{\min} = 0.980$, $T_{\max} = 0.995$

16063 measured reflections

4174 independent reflections

2653 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.8^\circ$

$h = -33 \rightarrow 32$

$k = -11 \rightarrow 11$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.119$

$S = 1.02$

4174 reflections

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

$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.9211P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

243 parameters

$$\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$$

0 restraints

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

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.46453 (5)	0.76202 (15)	0.40473 (7)	0.0576 (3)
O2	0.64520 (4)	0.88611 (14)	0.58892 (7)	0.0528 (3)
O3	0.69778 (5)	1.07722 (17)	0.52182 (8)	0.0604 (4)
N1	0.38948 (5)	0.63069 (15)	0.42694 (7)	0.0411 (3)
N2	0.37762 (5)	0.53986 (16)	0.49225 (8)	0.0418 (3)
N3	0.55797 (5)	0.72973 (16)	0.59800 (8)	0.0461 (3)
N4	0.55879 (5)	0.81534 (15)	0.52518 (8)	0.0400 (3)
C1	0.35469 (6)	0.63351 (18)	0.34260 (9)	0.0371 (3)
C2	0.32860 (6)	0.49921 (19)	0.30573 (10)	0.0431 (4)
H2	0.3357	0.4037	0.3339	0.052*
C3	0.29185 (6)	0.5090 (2)	0.22647 (11)	0.0490 (4)
H3	0.2730	0.4203	0.2022	0.059*
C4	0.28296 (6)	0.6486 (2)	0.18339 (10)	0.0504 (4)
H4	0.2579	0.6546	0.1303	0.060*
C5	0.31115 (7)	0.7800 (2)	0.21888 (11)	0.0497 (4)
H5	0.3061	0.8736	0.1886	0.060*
C6	0.34670 (6)	0.77364 (19)	0.29874 (10)	0.0440 (4)
H6	0.3652	0.8629	0.3230	0.053*
C7	0.44219 (6)	0.68619 (19)	0.45316 (9)	0.0405 (4)
C8	0.46208 (6)	0.63199 (18)	0.53974 (9)	0.0379 (3)
C9	0.42086 (6)	0.54514 (18)	0.56011 (9)	0.0391 (4)
C10	0.51460 (6)	0.6533 (2)	0.59932 (9)	0.0455 (4)
H10	0.5176	0.5990	0.6505	0.055*
C11	0.60540 (6)	0.89180 (17)	0.52552 (9)	0.0381 (3)
C12	0.60884 (6)	0.98077 (18)	0.44780 (9)	0.0384 (4)
C13	0.65628 (6)	1.06824 (19)	0.45021 (10)	0.0423 (4)
C14	0.66193 (7)	1.1489 (2)	0.37797 (11)	0.0520 (4)
H14	0.6933	1.2075	0.3802	0.062*
C15	0.62176 (8)	1.1429 (2)	0.30318 (11)	0.0545 (4)
H15	0.6261	1.1964	0.2548	0.065*

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C16	0.57499 (8)	1.0581 (2)	0.29950 (11)	0.0567 (5)
H16	0.5478	1.0541	0.2487	0.068*
C17	0.56846 (7)	0.9792 (2)	0.37078 (10)	0.0495 (4)
H17	0.5364	0.9235	0.3678	0.059*
C18	0.32105 (7)	0.5084 (2)	0.49384 (11)	0.0549 (5)
H18A	0.3183	0.5003	0.5524	0.082*
H18B	0.3094	0.4122	0.4644	0.082*
H18C	0.2982	0.5921	0.4658	0.082*
C19	0.42026 (7)	0.4633 (2)	0.64200 (10)	0.0536 (4)
H19A	0.3935	0.3815	0.6307	0.080*
H19B	0.4113	0.5365	0.6818	0.080*
H19C	0.4556	0.4193	0.6662	0.080*
H4N	0.5272 (7)	0.812 (2)	0.4759 (11)	0.064*
H3O	0.6855 (9)	1.012 (2)	0.5610 (13)	0.080*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0432 (6)	0.0856 (9)	0.0391 (6)	-0.0239 (6)	0.0004 (5)	0.0156 (6)
O2	0.0401 (6)	0.0670 (8)	0.0431 (6)	-0.0113 (6)	-0.0058 (5)	0.0095 (5)
O3	0.0418 (7)	0.0787 (9)	0.0547 (8)	-0.0157 (6)	0.0001 (6)	0.0107 (6)
N1	0.0359 (7)	0.0532 (8)	0.0339 (7)	-0.0077 (6)	0.0080 (5)	0.0031 (6)
N2	0.0380 (7)	0.0511 (8)	0.0388 (7)	-0.0065 (6)	0.0141 (6)	0.0016 (6)
N3	0.0427 (8)	0.0572 (9)	0.0342 (7)	-0.0076 (7)	0.0010 (6)	0.0060 (6)
N4	0.0358 (7)	0.0470 (8)	0.0331 (7)	-0.0045 (6)	0.0001 (5)	0.0042 (6)
C1	0.0298 (7)	0.0484 (9)	0.0334 (7)	-0.0019 (6)	0.0083 (6)	-0.0051 (7)
C2	0.0414 (9)	0.0445 (9)	0.0440 (9)	-0.0030 (7)	0.0117 (7)	-0.0051 (7)
C3	0.0409 (9)	0.0573 (11)	0.0488 (10)	-0.0091 (8)	0.0111 (8)	-0.0149 (8)
C4	0.0360 (9)	0.0707 (13)	0.0406 (9)	0.0002 (8)	0.0021 (7)	-0.0055 (8)
C5	0.0464 (10)	0.0539 (11)	0.0466 (9)	0.0041 (8)	0.0073 (8)	0.0046 (8)
C6	0.0422 (9)	0.0451 (10)	0.0439 (9)	-0.0052 (7)	0.0088 (7)	-0.0046 (7)
C7	0.0368 (8)	0.0485 (9)	0.0346 (8)	-0.0068 (7)	0.0058 (6)	-0.0012 (7)
C8	0.0376 (8)	0.0437 (9)	0.0325 (8)	-0.0018 (7)	0.0084 (6)	-0.0025 (6)
C9	0.0407 (8)	0.0431 (9)	0.0354 (8)	-0.0003 (7)	0.0130 (7)	-0.0025 (6)
C10	0.0451 (9)	0.0570 (11)	0.0322 (8)	-0.0048 (8)	0.0053 (7)	0.0058 (7)
C11	0.0341 (8)	0.0388 (8)	0.0377 (8)	-0.0008 (6)	0.0014 (6)	-0.0019 (6)
C12	0.0361 (8)	0.0382 (9)	0.0387 (8)	0.0016 (6)	0.0046 (7)	0.0006 (6)
C13	0.0382 (8)	0.0425 (9)	0.0439 (9)	-0.0007 (7)	0.0058 (7)	-0.0001 (7)
C14	0.0512 (10)	0.0506 (11)	0.0555 (10)	-0.0083 (8)	0.0157 (8)	0.0043 (8)
C15	0.0652 (12)	0.0527 (11)	0.0464 (10)	-0.0001 (9)	0.0155 (9)	0.0086 (8)
C16	0.0574 (11)	0.0642 (12)	0.0414 (10)	-0.0053 (9)	-0.0017 (8)	0.0081 (8)
C17	0.0448 (9)	0.0551 (11)	0.0436 (9)	-0.0078 (8)	0.0011 (7)	0.0065 (8)
C18	0.0400 (9)	0.0760 (13)	0.0515 (10)	-0.0125 (9)	0.0167 (8)	0.0009 (9)
C19	0.0559 (11)	0.0632 (12)	0.0440 (9)	-0.0041 (9)	0.0165 (8)	0.0081 (8)

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

O1—C7	1.2469 (18)	C6—H6	0.9300
O2—C11	1.2445 (17)	C7—C8	1.434 (2)

O3—C13	1.3553 (18)	C8—C9	1.381 (2)
O3—H3O	0.95 (2)	C8—C10	1.445 (2)
N1—C7	1.3785 (19)	C9—C19	1.492 (2)
N1—N2	1.3940 (17)	C10—H10	0.9300
N1—C1	1.4225 (18)	C11—C12	1.481 (2)
N2—C9	1.3417 (19)	C12—C17	1.397 (2)
N2—C18	1.4588 (19)	C12—C13	1.405 (2)
N3—C10	1.280 (2)	C13—C14	1.385 (2)
N3—N4	1.3830 (17)	C14—C15	1.370 (2)
N4—C11	1.3450 (19)	C14—H14	0.9300
N4—H4N	0.978 (18)	C15—C16	1.375 (2)
C1—C6	1.381 (2)	C15—H15	0.9300
C1—C2	1.384 (2)	C16—C17	1.371 (2)
C2—C3	1.382 (2)	C16—H16	0.9300
C2—H2	0.9300	C17—H17	0.9300
C3—C4	1.372 (2)	C18—H18A	0.9600
C3—H3	0.9300	C18—H18B	0.9600
C4—C5	1.378 (2)	C18—H18C	0.9600
C4—H4	0.9300	C19—H19A	0.9600
C5—C6	1.375 (2)	C19—H19B	0.9600
C5—H5	0.9300	C19—H19C	0.9600
C13—O3—H3O	102.6 (13)	C8—C9—C19	129.08 (14)
C7—N1—N2	109.30 (12)	N3—C10—C8	134.81 (14)
C7—N1—C1	127.67 (12)	N3—C10—H10	112.6
N2—N1—C1	121.87 (12)	C8—C10—H10	112.6
C9—N2—N1	108.03 (12)	O2—C11—N4	121.06 (14)
C9—N2—C18	126.78 (13)	O2—C11—C12	120.45 (13)
N1—N2—C18	120.37 (13)	N4—C11—C12	118.47 (13)
C10—N3—N4	118.23 (13)	C17—C12—C13	117.59 (14)
C11—N4—N3	116.54 (12)	C17—C12—C11	124.04 (14)
C11—N4—H4N	124.0 (11)	C13—C12—C11	118.34 (13)
N3—N4—H4N	119.4 (11)	O3—C13—C14	117.70 (14)
C6—C1—C2	120.59 (14)	O3—C13—C12	122.12 (14)
C6—C1—N1	118.62 (13)	C14—C13—C12	120.18 (15)
C2—C1—N1	120.77 (14)	C15—C14—C13	120.58 (16)
C3—C2—C1	119.07 (15)	C15—C14—H14	119.7
C3—C2—H2	120.5	C13—C14—H14	119.7
C1—C2—H2	120.5	C14—C15—C16	120.14 (16)
C4—C3—C2	120.46 (15)	C14—C15—H15	119.9
C4—C3—H3	119.8	C16—C15—H15	119.9
C2—C3—H3	119.8	C17—C16—C15	119.99 (16)
C3—C4—C5	119.91 (15)	C17—C16—H16	120.0
C3—C4—H4	120.0	C15—C16—H16	120.0
C5—C4—H4	120.0	C16—C17—C12	121.51 (16)
C6—C5—C4	120.50 (16)	C16—C17—H17	119.2
C6—C5—H5	119.8	C12—C17—H17	119.2
C4—C5—H5	119.8	N2—C18—H18A	109.5
C5—C6—C1	119.35 (15)	N2—C18—H18B	109.5
C5—C6—H6	120.3	H18A—C18—H18B	109.5

supplementary materials

C1—C6—H6	120.3	N2—C18—H18C	109.5
O1—C7—N1	122.57 (13)	H18A—C18—H18C	109.5
O1—C7—C8	131.79 (14)	H18B—C18—H18C	109.5
N1—C7—C8	105.59 (13)	C9—C19—H19A	109.5
C9—C8—C7	107.25 (13)	C9—C19—H19B	109.5
C9—C8—C10	122.31 (14)	H19A—C19—H19B	109.5
C7—C8—C10	130.42 (14)	C9—C19—H19C	109.5
N2—C9—C8	109.73 (13)	H19A—C19—H19C	109.5
N2—C9—C19	121.19 (14)	H19B—C19—H19C	109.5
C7—N1—N2—C9	3.35 (17)	N1—N2—C9—C19	178.01 (14)
C1—N1—N2—C9	171.97 (13)	C18—N2—C9—C19	22.9 (2)
C7—N1—N2—C18	160.36 (14)	C7—C8—C9—N2	1.00 (18)
C1—N1—N2—C18	-31.0 (2)	C10—C8—C9—N2	-177.66 (14)
C10—N3—N4—C11	-178.83 (15)	C7—C8—C9—C19	-179.73 (16)
C7—N1—C1—C6	-52.2 (2)	C10—C8—C9—C19	1.6 (3)
N2—N1—C1—C6	141.46 (14)	N4—N3—C10—C8	-0.2 (3)
C7—N1—C1—C2	128.96 (17)	C9—C8—C10—N3	-177.33 (18)
N2—N1—C1—C2	-37.4 (2)	C7—C8—C10—N3	4.4 (3)
C6—C1—C2—C3	-3.9 (2)	N3—N4—C11—O2	-0.7 (2)
N1—C1—C2—C3	175.00 (13)	N3—N4—C11—C12	178.00 (13)
C1—C2—C3—C4	2.6 (2)	O2—C11—C12—C17	172.71 (15)
C2—C3—C4—C5	0.5 (2)	N4—C11—C12—C17	-6.0 (2)
C3—C4—C5—C6	-2.4 (2)	O2—C11—C12—C13	-5.1 (2)
C4—C5—C6—C1	1.1 (2)	N4—C11—C12—C13	176.17 (14)
C2—C1—C6—C5	2.0 (2)	C17—C12—C13—O3	179.98 (15)
N1—C1—C6—C5	-176.85 (14)	C11—C12—C13—O3	-2.1 (2)
N2—N1—C7—O1	175.00 (15)	C17—C12—C13—C14	-0.1 (2)
C1—N1—C7—O1	7.2 (3)	C11—C12—C13—C14	177.82 (15)
N2—N1—C7—C8	-2.66 (17)	O3—C13—C14—C15	179.16 (16)
C1—N1—C7—C8	-170.43 (14)	C12—C13—C14—C15	-0.8 (3)
O1—C7—C8—C9	-176.30 (18)	C13—C14—C15—C16	0.8 (3)
N1—C7—C8—C9	1.05 (17)	C14—C15—C16—C17	0.1 (3)
O1—C7—C8—C10	2.2 (3)	C15—C16—C17—C12	-1.0 (3)
N1—C7—C8—C10	179.56 (16)	C13—C12—C17—C16	1.0 (3)
N1—N2—C9—C8	-2.65 (17)	C11—C12—C17—C16	-176.83 (16)
C18—N2—C9—C8	-157.76 (16)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3O \cdots O2	0.95 (2)	1.62 (2)	2.5076 (17)	155 (2)
N4—H4N \cdots O1	0.978 (18)	1.763 (18)	2.7140 (16)	163.3 (16)

Fig. 1

