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4-{(*E*)-[(2-Hydroxynaphthalen-1-yl)methylidene]-amino}-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one: a new polymorph (*β*-phase)

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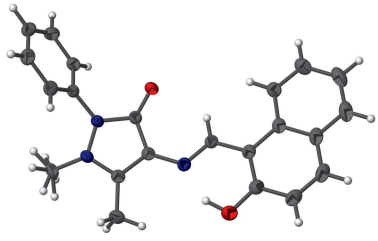
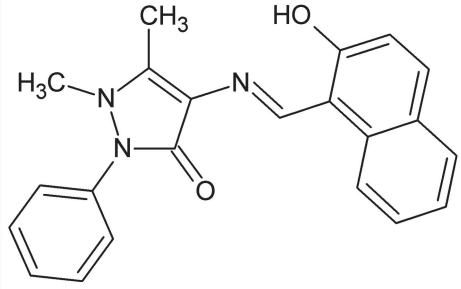
Structural data: full structural data are available from iucrdata.iucr.org

The title molecule, $C_{22}H_{19}N_3O_2$, is a new polymorphic modification, *viz*. the *β*-phase; the *α*-phase has been previously published [Liang & Wang (2010). *Acta Cryst*. E**66**, o1968–o1969]. In the crystal of the *β*-phase, the molecules pack in helical chains generated by C—H···O hydrogen bonds and offset *π*–*π*-stacking interactions. Adjacent chains are associated through C—H···*π* interactions. In the *α*-phase, molecules are linked by C—H···O and N—H···O hydrogen bonds, forming layers parallel to the $(10\overline{2})$ plane. In addition, *π*–*π*-stacking interactions and C—H···*π*(ring) interactions consolidate the packing. The packing is compared to that of the *α*-phase. The title compound was refined as a two-component twin.

3D view



Chemical scheme



Structure description

The chemistry of pyrazolone has gained increasing attention due to its diverse pharmacological properties such as cytotoxic, anti-inflammatory, antimicrobial, antioxidant, antifungal, antiviral, oral hypoglycaemic activity (Kumar *et al.*, 2012). One of the most significant pyrazolone derivatives is antipyrine. Antipyrine derivatives are reported to exhibit analgesic and anti-inflammatory effects, antiviral and antibacterial activities and have also been used as hair-color additives and to increase the local anesthetic effect of lidocaine (Anupama *et al.*, 2012). Schiff bases of 4-aminoantipyrine and their metal complexes have a variety of applications in biological, analytical and pharmacological areas. Studies of new kinds of chemotherapeutic Schiff bases are now attracting the

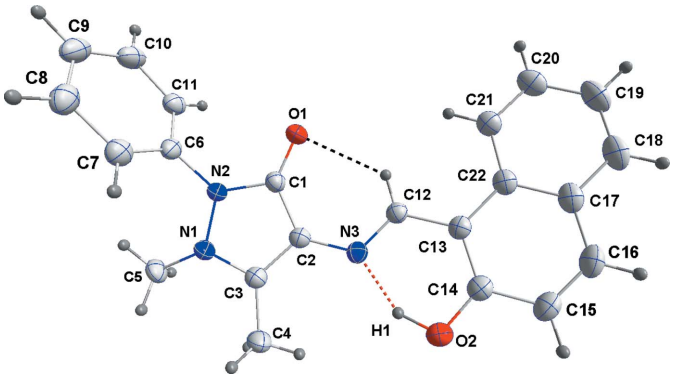


Figure 1
The title molecule with labeling scheme and 50% probability ellipsoids.

attention of biochemists (Shakru, 2015). In light of these facts and as a continuation of our work on the synthesis of Schiff bases and hydrazones of the biological active nucleus (Mohamed *et al.*, 2015), the title compound was synthesized. Here, we present the crystal structure of a new polymorph (Fig. 1), which we have called the β-phase. The α-phase corresponds to the crystal form reported earlier (Liang & Wang, 2010).

The β-phase crystallizes in the monoclinic space group $P2_1/c$, with a = 13.7321 (3), b = 6.7719 (2), c = 19.1916 (4) Å, β = 99.428 (1) °, V = 1760.57 (7) Å^3 and Z = 4 (Table 2), while the α-phase crystallizes in the same space group, with a = 8.0636 (7), b = 7.4407 (6), c = 30.169 (3) Å, β = 94.329 (2)°, V = 1804.9 (3) Å^3, Z = 4. The bond lengths and bond angles in the β-phase are in good agreement with the values observed in the α-phase. The C11—C6—N2—N1 and C7—C6—N2—C1 torsion angles are 146.38 (12) and 107.37 (15)°, respectively. In the α-phase, the corresponding angles are similar [147.2 (2) and 115.1 (2)°, respectively].

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1···N3	1.00 (2)	1.64 (2)	2.5502 (14)	150 (2)
C4—H4B···O1^{i}	0.98	2.55	3.5049 (18)	166
C5—H5A···O2^{ii}	0.98	2.52	3.3923 (17)	148
C12—H12···O1	0.95	2.32	2.9978 (16)	128

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

In the β-phase, the mean planes of the phenyl ring and the naphthalene moiety make dihedral angles of 56.97 (7) and 12.14 (6)°, respectively, with that of the central heterocyclic ring, while in the α-phase, the corresponding dihedral angles are 50.39 (13) and 11.62 (10)°. The dihedral angles between the mean planes of the phenyl ring and the naphthalene ring system in the α- and β-phases are 61.81 (10) and 64.63 (5)°, respectively.

In the β-phase (Fig. 1), the conformation is partially determined by the intramolecular O2—H1···N3 and C12—H12···O1 hydrogen bonds (Table 1). In the crystal, the molecules form helical chains along the 2_1 axes which involve C4—H4B···O1^{i} and C5—H5A···O2^{ii} [symmetry codes: (i) x, $y+1$, z; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$] (Table 1 and Fig. 2) as well as pairwise, offset π–π-stacking interactions between the C1–C3/N1/N2 and the C17–C22 rings across centers of symmetry (Fig. 3). In these, the distance between centroids is 3.889 (1) Å, the perpendicular distance between the rings is 3.254 (1) Å and the slippage is 1.53 Å. C9—H9···π(ring) interactions with the benzene ring in an adjacent chain (H9···centroid = 2.73 Å; C9—H9···centroid = 140°; Fig. 3) tie the chains together.

In the α-phase (Fig. 4), the molecular conformation is also partially determined by the intramolecular O—H···N [2.569 (2) Å, 148°] and C—H···O [3.083 (3) Å, 128°] hydrogen bonds.

In the crystal of the β-phase, the molecules form helical chains along the 2_1 axes which involve C—H···O and C—

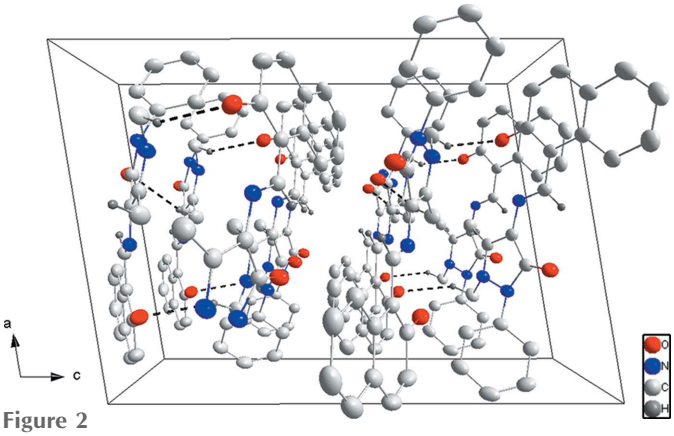


Figure 2
Packing viewed along the b axis with C—H···O hydrogen bonds shown as dotted lines.

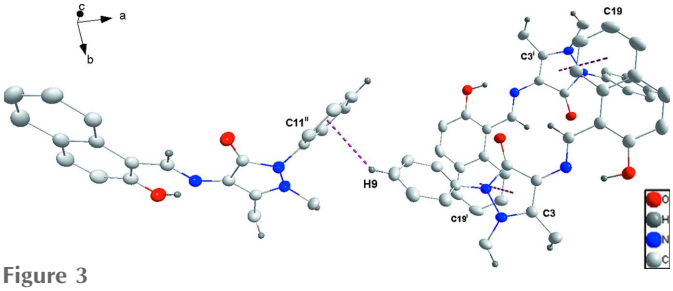


Figure 3
Detail of the offset π-π-stacking and the C—H···π interaction [symmetry code (i): $1-x, 1-y, 1-z$; (ii): $-x, -\frac{1}{2}+y, \frac{1}{2}-z$].

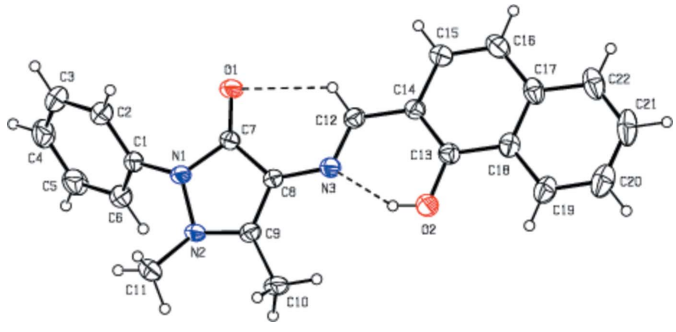


Figure 4
The molecule of the α-phase with labeling scheme and 30% probability ellipsoids.

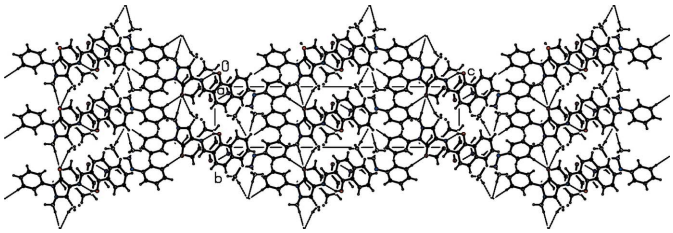


Figure 5
Packing viewed along the *a* axis of of the α-phase.

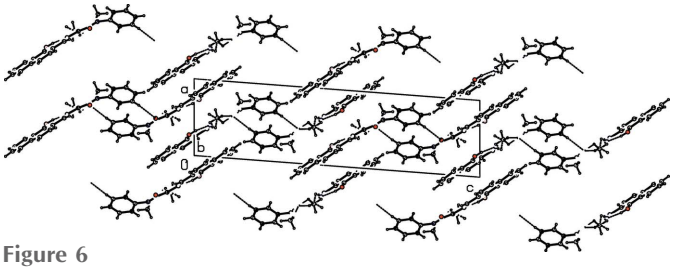


Figure 6
Packing viewed along the *b* axis of of the α-phase.

H···O (Table 1 and Fig. 2) as well as pairwise, offset π–π-stacking interactions (Fig. 3). C—H···π(ring) interactions with the benzene ring in an adjacent chain (Fig. 3) tie the chains together. In the crystal of the α-phase (Figs. 5 and 6), molecules are linked by C—H···O and N—H···O hydrogen bonds, forming layers parallel to the $(10\overline{2})$ plane. In addition, π–π-stacking interactions and C—H···π(ring) interactions contribute to the molecular packing.

Synthesis and crystallization

A mixture of 1 mmol (203 mg) of 4-aminoantipyrine and 1 mmol (172 mg) of 2-hydroxynaphthalene-1-carbaldehyde with a few drops of glacial acetic acid was refluxed in 25 ml of absolute ethanol for 6 h. The mixture was cooled and left for evaporation at room temperature. The solid was collected and recrystallized from ethanol to afford yellow crystals of good quality for X-ray diffraction with m.p = 485–488 K.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The title compound was refined as a two-component twin. The H atoms of the methyl group (C5) were refined as disordered over two sets of atomic sites in a 0.57 (2):0.43 (2) ratio.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{19}N_3O_2$
M_r	357.40
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	13.7321 (3), 6.7719 (2), 19.1916 (4)
β (°)	99.428 (1)
V (Å^3)	1760.57 (7)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.71
Crystal size (mm)	0.24 × 0.23 × 0.05
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON 100 CMOS
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 2009)
T_{min}, T_{max}	0.85, 0.96
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	69179, 6532, 5754
R_{int}	0.051
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.095, 1.04
No. of reflections	6532
No. of parameters	252
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.21, −0.16

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*b*), *SHELXL2014* (Sheldrick, 2015*a*), *DIAMOND* (Brandenburg & Putz, 2012), *PLATON* (Farrugia, 2012) and *SHELXTL* (Sheldrick, 2008).

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171166 [https://doi.org/10.1107/S2414314617011660X]

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4-{(*E*)-[(2-Hydroxynaphthalen-1-yl)methylidene]amino}-1,5-dimethyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-one

Crystal data

$C_{22}H_{19}N_3O_2$
M_r = 357.40
Monoclinic, $P2_1/c$
a = 13.7321 (3) Å
b = 6.7719 (2) Å
c = 19.1916 (4) Å
β = 99.428 (1)°
V = 1760.57 (7) Å^3
Z = 4
$F(000)$ = 752
D_x = 1.348 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9892 reflections
θ = 4.7–72.4°
μ = 0.71 mm^{-1}
T = 150 K
Plate, yellow
0.24 × 0.23 × 0.05 mm

Data collection

Bruker D8 VENTURE PHOTON 100 CMOS diffractometer
Radiation source: INCOATEC IμS micro-focus source
Mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2009)
T_{min} = 0.85, T_{max} = 0.96
69179 measured reflections
6532 independent reflections
5754 reflections with $I > 2\sigma(I)$
R_{int} = 0.051
θ_{max} = 72.5°, θ_{min} = 3.3°
h = −16→16
k = −8→8
l = −22→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.095
S = 1.04
6532 reflections
252 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0493P)^2 + 0.2553P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015*b*), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0063 (6)

Special details

Experimental. Analysis of 1195 reflections having I/σ(I) > 13 and chosen from the full data set with *CELL_NOW* (Sheldrick, 2008) showed the crystal to belong to the monoclinic system and to be twinned by a 180° rotation about the *c* axis. The raw data were processed using the multi-component version of *SAINT* under control of the two-component orientation file generated by *CELL_NOW*.

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 $F^2 > 2\text{sigma}(F^2)$ 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 - 0.98 Å) and included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.36874 (7)	0.43580 (13)	0.39097 (5)	0.0331 (2)	
H1	0.6674 (18)	0.768 (3)	0.3736 (12)	0.077 (7)*	
O2	0.74041 (7)	0.75220 (14)	0.37735 (5)	0.0343 (2)	
N1	0.32968 (8)	0.87923 (15)	0.30077 (6)	0.0288 (3)	
N2	0.29535 (8)	0.71017 (16)	0.33098 (6)	0.0278 (2)	
N3	0.55962 (8)	0.67844 (16)	0.38249 (6)	0.0263 (2)	
C1	0.37593 (9)	0.60272 (18)	0.36613 (7)	0.0256 (3)	
C2	0.46053 (9)	0.72526 (18)	0.36180 (6)	0.0251 (3)	
C3	0.42822 (9)	0.89174 (19)	0.32357 (7)	0.0265 (3)	
C4	0.48594 (11)	1.0662 (2)	0.30724 (8)	0.0354 (3)	
H4A	0.5562	1.0433	0.3245	0.053*	
H4B	0.4640	1.1832	0.3304	0.053*	
H4C	0.4757	1.0872	0.2560	0.053*	
C5	0.26206 (11)	1.0460 (2)	0.28403 (8)	0.0335 (3)	
H5A	0.2852	1.1298	0.2485	0.050*	0.651 (19)
H5B	0.2600	1.1234	0.3269	0.050*	0.651 (19)
H5C	0.1958	0.9966	0.2655	0.050*	0.651 (19)
H5D	0.2095	1.0382	0.3129	0.050*	0.349 (19)
H5E	0.2329	1.0415	0.2339	0.050*	0.349 (19)
H5F	0.2984	1.1700	0.2941	0.050*	0.349 (19)
C6	0.20697 (9)	0.61651 (18)	0.29731 (7)	0.0265 (3)	
C7	0.18437 (10)	0.6067 (2)	0.22427 (7)	0.0316 (3)	
H7	0.2261	0.6672	0.1956	0.038*	
C8	0.09971 (11)	0.5071 (2)	0.19373 (8)	0.0360 (3)	
H8	0.0828	0.5010	0.1438	0.043*	
C9	0.03978 (10)	0.4165 (2)	0.23564 (9)	0.0383 (3)	
H9	−0.0178	0.3479	0.2144	0.046*	
C10	0.06376 (10)	0.4259 (2)	0.30848 (9)	0.0370 (3)	
H10	0.0229	0.3623	0.3371	0.044*	
C11	0.14726 (10)	0.52779 (19)	0.33982 (8)	0.0308 (3)	

H11	0.1632	0.5366	0.3898	0.037*
C12	0.58626 (9)	0.51723 (18)	0.41693 (7)	0.0259 (3)
H12	0.5375	0.4354	0.4321	0.031*
C13	0.68951 (9)	0.45992 (19)	0.43270 (7)	0.0265 (3)
C14	0.76203 (10)	0.5805 (2)	0.41184 (7)	0.0295 (3)
C15	0.86264 (10)	0.5260 (2)	0.42589 (8)	0.0367 (3)
H15	0.9110	0.6091	0.4110	0.044*
C16	0.89041 (10)	0.3553 (2)	0.46066 (8)	0.0381 (3)
H16	0.9585	0.3218	0.4703	0.046*
C17	0.82053 (10)	0.2258 (2)	0.48297 (7)	0.0327 (3)
C18	0.84983 (12)	0.0482 (2)	0.51936 (8)	0.0410 (4)
H18	0.9180	0.0161	0.5299	0.049*
C19	0.78211 (13)	−0.0777 (2)	0.53952 (8)	0.0425 (4)
H19	0.8031	−0.1965	0.5637	0.051*
C20	0.68136 (12)	−0.0308 (2)	0.52439 (8)	0.0378 (3)
H20	0.6341	−0.1192	0.5380	0.045*
C21	0.65050 (10)	0.1412 (2)	0.49018 (7)	0.0314 (3)
H21	0.5820	0.1706	0.4808	0.038*
C22	0.71852 (10)	0.2764 (2)	0.46839 (6)	0.0277 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0305 (5)	0.0246 (5)	0.0428 (6)	−0.0014 (4)	0.0021 (4)	0.0081 (4)
O2	0.0326 (5)	0.0340 (5)	0.0376 (5)	−0.0029 (4)	0.0094 (4)	0.0045 (4)
N1	0.0295 (6)	0.0210 (5)	0.0343 (6)	−0.0006 (4)	0.0005 (5)	0.0045 (4)
N2	0.0270 (5)	0.0216 (5)	0.0332 (6)	−0.0013 (4)	0.0002 (4)	0.0037 (4)
N3	0.0260 (5)	0.0268 (6)	0.0257 (5)	−0.0003 (4)	0.0030 (4)	−0.0009 (4)
C1	0.0270 (6)	0.0231 (6)	0.0261 (6)	0.0014 (5)	0.0027 (5)	−0.0002 (5)
C2	0.0267 (6)	0.0241 (6)	0.0245 (6)	−0.0002 (5)	0.0045 (5)	−0.0011 (5)
C3	0.0299 (6)	0.0245 (6)	0.0249 (6)	−0.0005 (5)	0.0042 (5)	−0.0016 (5)
C4	0.0380 (7)	0.0292 (7)	0.0380 (8)	−0.0046 (6)	0.0033 (6)	0.0065 (6)
C5	0.0372 (7)	0.0254 (7)	0.0357 (7)	0.0060 (6)	−0.0005 (6)	0.0047 (5)
C6	0.0235 (6)	0.0203 (6)	0.0344 (7)	0.0025 (5)	0.0008 (5)	−0.0015 (5)
C7	0.0298 (7)	0.0301 (7)	0.0347 (7)	0.0025 (5)	0.0048 (6)	−0.0014 (5)
C8	0.0347 (7)	0.0321 (7)	0.0384 (8)	0.0034 (6)	−0.0026 (6)	−0.0076 (6)
C9	0.0287 (7)	0.0269 (7)	0.0564 (9)	−0.0012 (5)	−0.0014 (6)	−0.0064 (6)
C10	0.0302 (7)	0.0280 (7)	0.0539 (9)	−0.0022 (5)	0.0099 (6)	0.0008 (6)
C11	0.0310 (7)	0.0244 (6)	0.0370 (7)	0.0029 (5)	0.0058 (6)	0.0007 (5)
C12	0.0257 (6)	0.0263 (6)	0.0254 (6)	−0.0012 (5)	0.0030 (5)	−0.0011 (5)
C13	0.0263 (6)	0.0288 (6)	0.0239 (6)	0.0000 (5)	0.0029 (5)	−0.0025 (5)
C14	0.0298 (7)	0.0319 (7)	0.0272 (6)	−0.0015 (5)	0.0054 (5)	−0.0029 (5)
C15	0.0269 (7)	0.0438 (8)	0.0401 (8)	−0.0031 (6)	0.0077 (6)	−0.0056 (6)
C16	0.0257 (6)	0.0475 (8)	0.0398 (8)	0.0059 (6)	0.0017 (6)	−0.0072 (7)
C17	0.0328 (7)	0.0368 (7)	0.0269 (6)	0.0073 (6)	0.0000 (5)	−0.0060 (6)
C18	0.0435 (8)	0.0435 (9)	0.0334 (8)	0.0167 (7)	−0.0011 (6)	−0.0041 (6)
C19	0.0607 (10)	0.0342 (8)	0.0310 (7)	0.0158 (7)	0.0032 (7)	0.0029 (6)
C20	0.0514 (9)	0.0321 (7)	0.0301 (7)	0.0028 (7)	0.0069 (6)	0.0009 (6)

C21	0.0356 (7)	0.0313 (7)	0.0266 (6)	0.0012 (6)	0.0028 (5)	−0.0002 (5)
C22	0.0305 (7)	0.0300 (6)	0.0217 (6)	0.0024 (5)	0.0019 (5)	−0.0040 (5)

Geometric parameters (Å, º)

O1—C1	1.2370 (15)	C8—C9	1.385 (2)
O2—C14	1.3465 (16)	C8—H8	0.9500
O2—H1	1.00 (2)	C9—C10	1.384 (2)
N1—C3	1.3549 (17)	C9—H9	0.9500
N1—N2	1.3996 (14)	C10—C11	1.388 (2)
N1—C5	1.4641 (16)	C10—H10	0.9500
N2—C1	1.4016 (16)	C11—H11	0.9500
N2—C6	1.4269 (16)	C12—C13	1.4533 (17)
N3—C12	1.2974 (16)	C12—H12	0.9500
N3—C2	1.3902 (16)	C13—C14	1.3963 (18)
C1—C2	1.4410 (18)	C13—C22	1.4434 (18)
C2—C3	1.3783 (17)	C14—C15	1.4127 (19)
C3—C4	1.4844 (18)	C15—C16	1.358 (2)
C4—H4A	0.9800	C15—H15	0.9500
C4—H4B	0.9800	C16—C17	1.417 (2)
C4—H4C	0.9800	C16—H16	0.9500
C5—H5A	0.9800	C17—C18	1.416 (2)
C5—H5B	0.9800	C17—C22	1.4245 (18)
C5—H5C	0.9800	C18—C19	1.363 (2)
C5—H5D	0.9801	C18—H18	0.9500
C5—H5E	0.9799	C19—C20	1.403 (2)
C5—H5F	0.9798	C19—H19	0.9500
C6—C11	1.3850 (19)	C20—C21	1.370 (2)
C6—C7	1.3866 (19)	C20—H20	0.9500
C7—C8	1.3883 (19)	C21—C22	1.4189 (19)
C7—H7	0.9500	C21—H21	0.9500
C14—O2—H1	105.6 (13)	C7—C8—H8	119.8
C3—N1—N2	107.68 (10)	C10—C9—C8	120.05 (13)
C3—N1—C5	125.91 (11)	C10—C9—H9	120.0
N2—N1—C5	118.52 (11)	C8—C9—H9	120.0
N1—N2—C1	109.34 (10)	C9—C10—C11	120.22 (14)
N1—N2—C6	119.68 (10)	C9—C10—H10	119.9
C1—N2—C6	122.21 (10)	C11—C10—H10	119.9
C12—N3—C2	121.23 (11)	C6—C11—C10	119.16 (13)
O1—C1—N2	123.59 (12)	C6—C11—H11	120.4
O1—C1—C2	131.64 (12)	C10—C11—H11	120.4
N2—C1—C2	104.69 (10)	N3—C12—C13	120.99 (12)
C3—C2—N3	123.59 (12)	N3—C12—H12	119.5
C3—C2—C1	108.03 (11)	C13—C12—H12	119.5
N3—C2—C1	127.79 (11)	C14—C13—C22	119.05 (12)
N1—C3—C2	109.77 (11)	C14—C13—C12	120.09 (12)
N1—C3—C4	121.41 (12)	C22—C13—C12	120.85 (12)

C2—C3—C4	128.83 (12)	O2—C14—C13	122.40 (12)
C3—C4—H4A	109.5	O2—C14—C15	116.70 (12)
C3—C4—H4B	109.5	C13—C14—C15	120.90 (13)
H4A—C4—H4B	109.5	C16—C15—C14	120.22 (14)
C3—C4—H4C	109.5	C16—C15—H15	119.9
H4A—C4—H4C	109.5	C14—C15—H15	119.9
H4B—C4—H4C	109.5	C15—C16—C17	121.73 (13)
N1—C5—H5A	109.5	C15—C16—H16	119.1
N1—C5—H5B	109.4	C17—C16—H16	119.1
H5A—C5—H5B	109.5	C18—C17—C16	121.54 (14)
N1—C5—H5C	109.5	C18—C17—C22	119.47 (14)
H5A—C5—H5C	109.5	C16—C17—C22	119.00 (13)
H5B—C5—H5C	109.5	C19—C18—C17	121.28 (14)
N1—C5—H5D	109.5	C19—C18—H18	119.4
N1—C5—H5E	109.5	C17—C18—H18	119.4
H5D—C5—H5E	109.4	C18—C19—C20	119.69 (14)
N1—C5—H5F	109.5	C18—C19—H19	120.2
H5D—C5—H5F	109.5	C20—C19—H19	120.2
H5E—C5—H5F	109.5	C21—C20—C19	120.58 (15)
C11—C6—C7	121.24 (12)	C21—C20—H20	119.7
C11—C6—N2	117.89 (12)	C19—C20—H20	119.7
C7—C6—N2	120.80 (12)	C20—C21—C22	121.53 (14)
C6—C7—C8	118.91 (13)	C20—C21—H21	119.2
C6—C7—H7	120.5	C22—C21—H21	119.2
C8—C7—H7	120.5	C21—C22—C17	117.43 (12)
C9—C8—C7	120.42 (14)	C21—C22—C13	123.48 (12)
C9—C8—H8	119.8	C17—C22—C13	119.09 (12)

C3—N1—N2—C1	−7.40 (14)	C7—C6—C11—C10	0.56 (19)
C5—N1—N2—C1	−158.31 (11)	N2—C6—C11—C10	−176.36 (12)
C3—N1—N2—C6	−155.64 (11)	C9—C10—C11—C6	−1.2 (2)
C5—N1—N2—C6	53.45 (16)	C2—N3—C12—C13	174.24 (11)
N1—N2—C1—O1	−171.60 (12)	N3—C12—C13—C14	1.11 (19)
C6—N2—C1—O1	−24.3 (2)	N3—C12—C13—C22	−177.35 (11)
N1—N2—C1—C2	5.62 (13)	C22—C13—C14—O2	178.92 (11)
C6—N2—C1—C2	152.90 (12)	C12—C13—C14—O2	0.43 (19)
C12—N3—C2—C3	−178.23 (12)	C22—C13—C14—C15	−0.69 (19)
C12—N3—C2—C1	−8.1 (2)	C12—C13—C14—C15	−179.17 (12)
O1—C1—C2—C3	175.00 (14)	O2—C14—C15—C16	179.79 (12)
N2—C1—C2—C3	−1.89 (14)	C13—C14—C15—C16	−0.6 (2)
O1—C1—C2—N3	3.7 (2)	C14—C15—C16—C17	0.9 (2)
N2—C1—C2—N3	−173.22 (12)	C15—C16—C17—C18	−179.83 (13)
N2—N1—C3—C2	6.14 (14)	C15—C16—C17—C22	0.1 (2)
C5—N1—C3—C2	154.30 (12)	C16—C17—C18—C19	−178.73 (14)
N2—N1—C3—C4	−173.52 (12)	C22—C17—C18—C19	1.3 (2)
C5—N1—C3—C4	−25.4 (2)	C17—C18—C19—C20	−0.3 (2)
N3—C2—C3—N1	169.14 (11)	C18—C19—C20—C21	−0.7 (2)
C1—C2—C3—N1	−2.64 (14)	C19—C20—C21—C22	0.6 (2)

N3—C2—C3—C4	−11.2 (2)	C20—C21—C22—C17	0.46 (19)
C1—C2—C3—C4	176.99 (13)	C20—C21—C22—C13	−179.51 (12)
N1—N2—C6—C11	−146.38 (12)	C18—C17—C22—C21	−1.39 (18)
C1—N2—C6—C11	69.57 (16)	C16—C17—C22—C21	178.69 (12)
N1—N2—C6—C7	36.68 (17)	C18—C17—C22—C13	178.58 (12)
C1—N2—C6—C7	−107.37 (15)	C16—C17—C22—C13	−1.34 (18)
C11—C6—C7—C8	0.5 (2)	C14—C13—C22—C21	−178.40 (12)
N2—C6—C7—C8	177.35 (12)	C12—C13—C22—C21	0.07 (19)
C6—C7—C8—C9	−1.0 (2)	C14—C13—C22—C17	1.63 (18)
C7—C8—C9—C10	0.4 (2)	C12—C13—C22—C17	−179.89 (11)
C8—C9—C10—C11	0.7 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H1···N3	1.00 (2)	1.64 (2)	2.5502 (14)	150 (2)
C4—H4*B*···O1^{i}	0.98	2.55	3.5049 (18)	166
C5—H5*A*···O2^{ii}	0.98	2.52	3.3923 (17)	148
C12—H12···O1	0.95	2.32	2.9978 (16)	128

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