

5-(Phenyldiazenyl)tropolone

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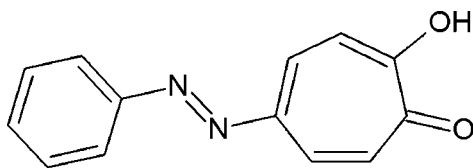
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.048; wR factor = 0.128; data-to-parameter ratio = 17.2.

The title compound [systematic name: (*E*)-2-hydroxy-5-(phenyldiazenyl)cyclohepta-2,4,6-trien-1-one], $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$, is essentially planar with an r.m.s. deviation of 0.036 (2) Å and a dihedral angle of 1.57 (8)° between the phenyl and tropolone rings. In the crystal, molecules are linked by pairs of O—H...O hydrogen bonds into inversion dimers. The dimers are further connected by C—H...O hydrogen bonds and π - π stacking interactions, with centroid-centroid distances of 3.6934 (9) and 3.6282 (9) Å.

Related literature

For synthetic background, see: Gao & Zheng (2001). For applications of azo-substituted tropolones, see: Mori *et al.* (2002). For related systems, see: Shimanouchi & Sasada (1973); Steyl & Roodt (2006). For a description of the Cambridge Structural Database, see: Allen (2002).



Experimental

Crystal data

 $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$ $M_r = 226.23$ Monoclinic, $P2_1/c$ $a = 6.2838$ (2) Å $b = 24.8474$ (13) Å $c = 8.0478$ (3) Å $\beta = 122.255$ (2)° $V = 1062.64$ (8) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.10$ mm⁻¹ $T = 100$ K

0.35 × 0.32 × 0.05 mm

Data collection

Bruker X8 APEXII 4K KappaCCD diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2004)

 $T_{\min} = 0.967$, $T_{\max} = 0.995$

10621 measured reflections

2669 independent reflections

1925 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.050$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.048$ $wR(F^2) = 0.128$ $S = 1.05$

2669 reflections

155 parameters

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1...O2	0.84	2.08	2.5754 (15)	117
C5—H5...O1 ⁱ	0.95	2.40	3.1866 (19)	140
O1—H1...O2 ⁱⁱ	0.84	1.96	2.6686 (15)	141

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

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT-Plus (Bruker, 2004); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg & Putz, 2005); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5073).

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supplementary materials

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Comment

Due to the special nature of the tropolone ring it demonstrates similar aromaticity as the benzene ring, undergoing electrophilic substitution reactions with electrophilic reagents. As part of our study on the functionlization of the tropolone moiety we report the structure of the title compound, **(I)** (Fig. 1), with the aim of contributing to a deeper understanding of troponoids and its functionlization. The original tropolone crystal structure was done by Shimanouchi & Sasada (1973). A search of the Cambridge structural database (CSD) (Allen, 2002) yielded thirteen troponoid compounds with a mono-substituted 5-position, of these only seven were with the tropolone backbone, none of which had an azo linking group.

In **I** the dihedral angle between the least-squares planes A (O1/O2/C1–C7/N1) and B (N2/C11–C16) was found to be 1.41 (6)°, resulting in an almost planar molecule with an *r.m.s.* deviation of 0.036 (2) Å. The largest variance from the molecular plane was found to be the O1 atom with a value of 0.058 (1) Å. The well known O—H···H interactions found for tropolone are present and lead to the formation of centrosymmetric dimers (Fig. 2). These interactions along with the last interaction found in Fig. 2, that of tropolone (C5) with an adjacent tropolone (O2) results in the formation of a planar sheet packing configuration (Fig 3). π – π Interactions were observed between the phenyl ring and the tropolone ring with a distance of 3.6934 (9) Å and two tropolone rings with a distance of 3.6282 (9) Å (Fig. 4).

Experimental

Sodium nitrite (1.4 mmol) dissolved in water (1 ml) was added dropwise to a solution containing aniline (1.6 mmol), hydrochloric acid (2 ml, conc) and water (7 ml). Upon cooling the resultant mixture to *ca.* 4 °C it was slowly added to a solution of sodium hydroxide (1.8 mmol), tropolone (1.6 mmol) in water (4 ml) keeping the temperature < 5 °C. The resulting solution was stirred for 30 minutes, filtered and air-dried. Crystals suitable for X-ray diffraction were obtained by recrystalization with CHCl₃.

Refinement

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINTE-Plus* (Bruker, 2004); data reduction: *SAINTE-Plus* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

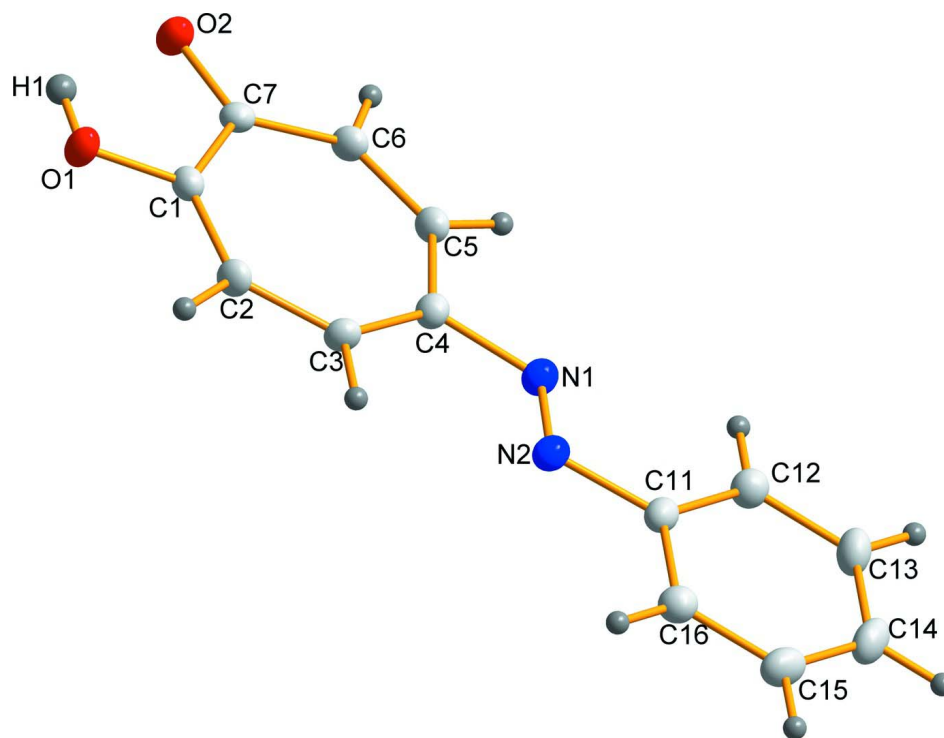


Figure 1

Molecular structure of the title compound (50% probability displacement ellipsoids).

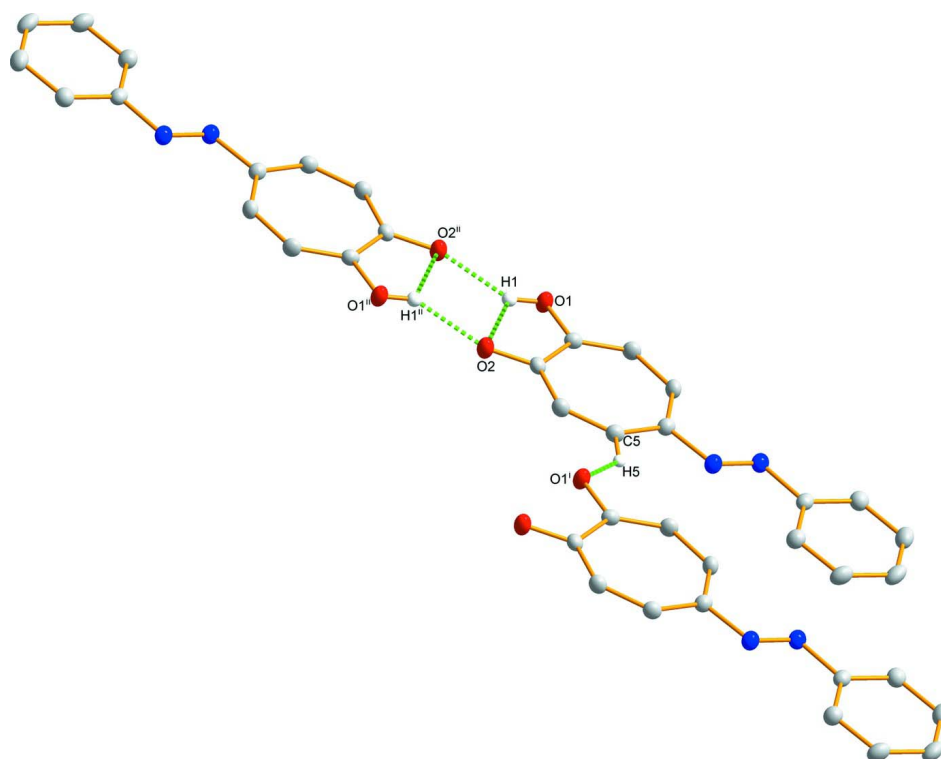


Figure 2

Intermolecular hydrogen bond interactions (dashed bonds) of the title compound. Symmetry codes: (i) $x - 1, y, z - 1$ (ii) $1 - x, -y, 3 - z$. Non-relevant hydrogen atoms have been omitted for clarity.

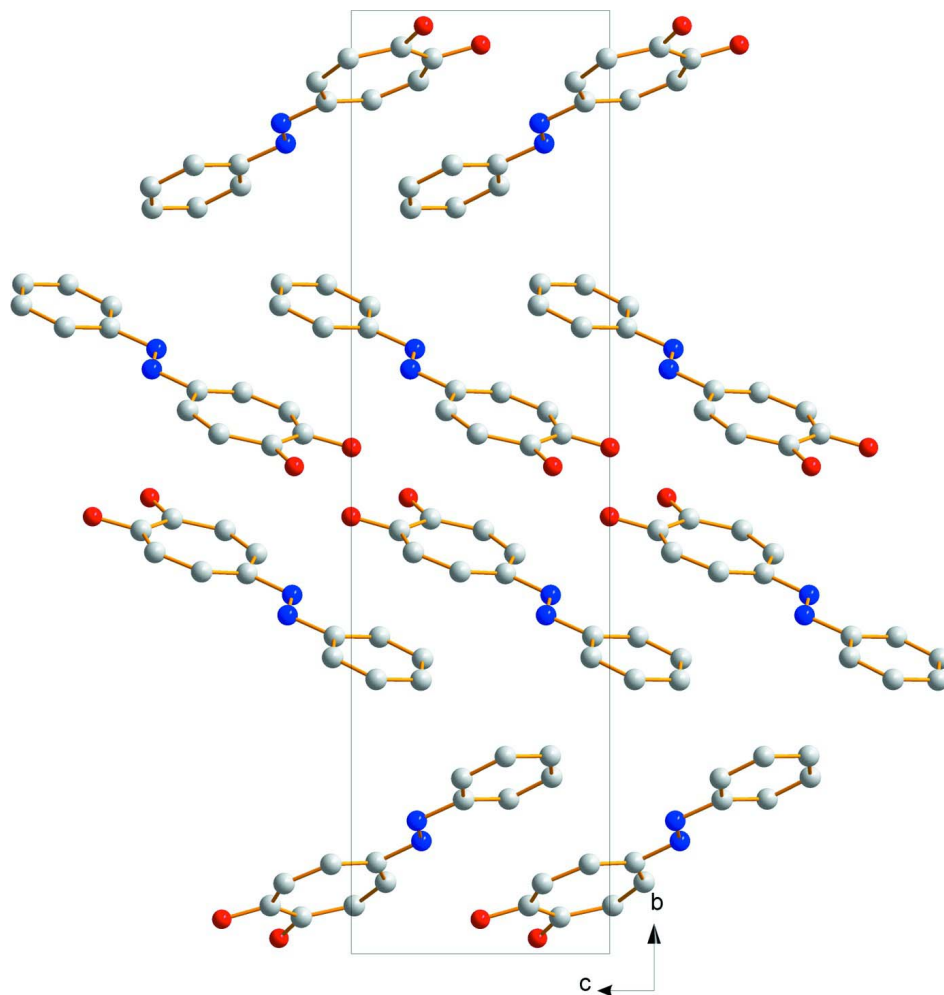
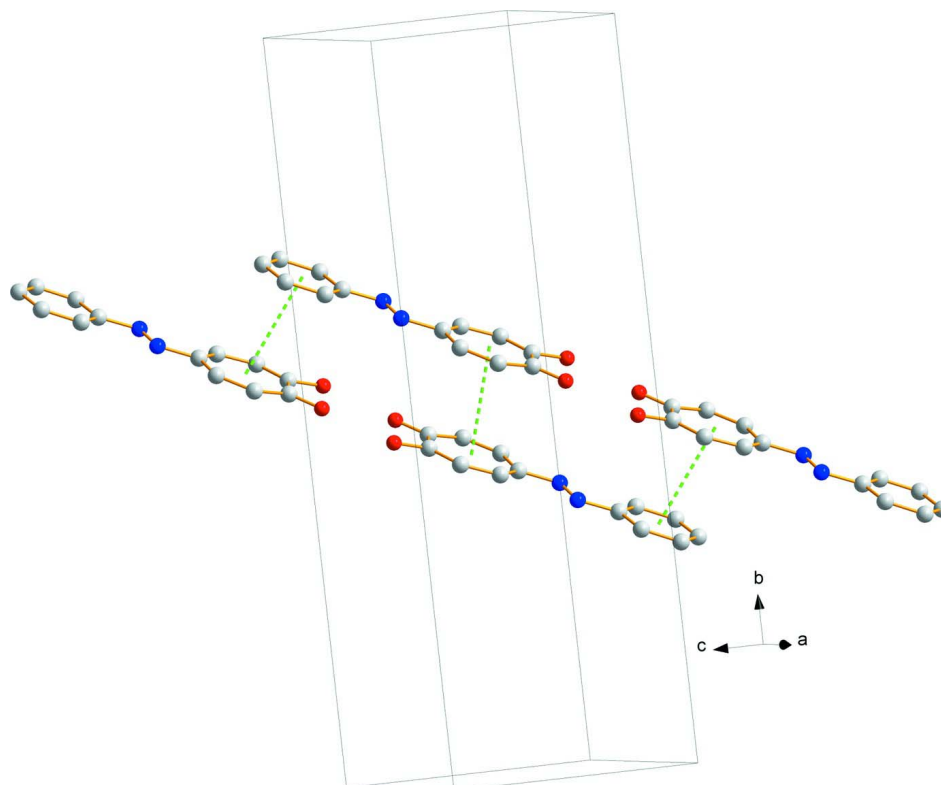


Figure 3

A packing diagram of the title compound, illustrating the parallel sheet configuration as viewed along the a axis.


Figure 4

Partially filled unit cell of the title compound, illustrating π - π stacking interactions. Hydrogen atoms have been omitted for clarity.

(E)-2-hydroxy-5-(phenyldiazenyl)cyclohepta-2,4,6-trien-1-one
Crystal data
 $C_{13}H_{10}N_2O_2$
 $M_r = 226.23$

 Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 6.2838 (2) \text{ \AA}$
 $b = 24.8474 (13) \text{ \AA}$
 $c = 8.0478 (3) \text{ \AA}$
 $\beta = 122.255 (2)^\circ$
 $V = 1062.64 (8) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 472$
 $D_x = 1.414 \text{ Mg m}^{-3}$

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

Cell parameters from 1666 reflections

 $\theta = 3.3\text{--}24.9^\circ$
 $\mu = 0.10 \text{ mm}^{-1}$
 $T = 100 \text{ K}$

Plate, red

 $0.35 \times 0.32 \times 0.05 \text{ mm}$
Data collection

 Bruker X8 APEXII 4K KappaCCD
diffractometer

Radiation source: sealed tube

Graphite monochromator

 Detector resolution: $512 \text{ pixels mm}^{-1}$
 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2004)

 $T_{\min} = 0.967, T_{\max} = 0.995$

10621 measured reflections

2669 independent reflections

 1925 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.050$
 $\theta_{\max} = 28.4^\circ, \theta_{\min} = 3.1^\circ$
 $h = -8 \rightarrow 8$
 $k = -31 \rightarrow 32$
 $l = -10 \rightarrow 10$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.128$
 $S = 1.05$
 2669 reflections
 155 parameters

0 restraints
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 0.2818P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.6923 (3)	0.05118 (6)	1.3134 (2)	0.0163 (3)
C2	0.8463 (3)	0.07450 (7)	1.2597 (2)	0.0179 (3)
H2	1.0185	0.077	1.3622	0.022*
C3	0.7891 (3)	0.09498 (7)	1.0787 (2)	0.0175 (3)
H3	0.9269	0.1095	1.0758	0.021*
C4	0.5591 (3)	0.09684 (7)	0.9038 (2)	0.0172 (3)
C5	0.3285 (3)	0.07598 (7)	0.8670 (2)	0.0177 (3)
H5	0.1911	0.08	0.7352	0.021*
C6	0.2696 (3)	0.05111 (7)	0.9882 (2)	0.0181 (4)
H6	0.099	0.04	0.9262	0.022*
C7	0.4217 (3)	0.03894 (6)	1.1931 (2)	0.0163 (3)
C11	0.6741 (3)	0.16352 (6)	0.5654 (2)	0.0178 (3)
C12	0.4382 (3)	0.16419 (7)	0.3910 (2)	0.0209 (4)
H12	0.2969	0.1489	0.3868	0.025*
C13	0.4112 (3)	0.18728 (7)	0.2241 (2)	0.0247 (4)
H13	0.251	0.1878	0.105	0.03*
C14	0.6179 (3)	0.20974 (7)	0.2304 (2)	0.0258 (4)
H14	0.5989	0.2255	0.1158	0.031*
C15	0.8514 (3)	0.20909 (7)	0.4036 (3)	0.0252 (4)
H15	0.9922	0.2246	0.4076	0.03*
C16	0.8811 (3)	0.18585 (7)	0.5718 (2)	0.0213 (4)
H16	1.0418	0.1852	0.6904	0.026*
N1	0.5284 (2)	0.11965 (6)	0.72852 (19)	0.0194 (3)
N2	0.7201 (3)	0.14104 (6)	0.74631 (18)	0.0196 (3)
O1	0.8030 (2)	0.03666 (5)	1.50085 (15)	0.0204 (3)
H1	0.6956	0.0231	1.5202	0.031*
O2	0.3290 (2)	0.01652 (5)	1.27961 (15)	0.0219 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0157 (8)	0.0170 (8)	0.0138 (7)	0.0017 (6)	0.0064 (6)	-0.0002 (6)
C2	0.0134 (8)	0.0216 (9)	0.0144 (7)	-0.0009 (6)	0.0046 (6)	-0.0004 (6)

C3	0.0162 (8)	0.0195 (9)	0.0185 (8)	-0.0022 (6)	0.0103 (7)	-0.0004 (6)
C4	0.0185 (8)	0.0174 (9)	0.0151 (7)	-0.0002 (6)	0.0087 (6)	-0.0003 (6)
C5	0.0154 (8)	0.0204 (9)	0.0142 (7)	0.0007 (6)	0.0058 (6)	-0.0006 (6)
C6	0.0139 (7)	0.0218 (9)	0.0162 (7)	-0.0007 (6)	0.0065 (6)	-0.0013 (6)
C7	0.0160 (8)	0.0170 (9)	0.0176 (7)	0.0008 (6)	0.0101 (6)	-0.0010 (6)
C11	0.0223 (8)	0.0149 (8)	0.0186 (8)	0.0008 (6)	0.0125 (7)	0.0004 (6)
C12	0.0217 (8)	0.0198 (9)	0.0214 (8)	-0.0015 (7)	0.0115 (7)	0.0003 (6)
C13	0.0296 (9)	0.0216 (10)	0.0192 (8)	0.0011 (7)	0.0105 (7)	0.0037 (7)
C14	0.0387 (10)	0.0183 (9)	0.0244 (9)	-0.0006 (8)	0.0195 (8)	0.0037 (7)
C15	0.0315 (10)	0.0197 (9)	0.0324 (9)	-0.0029 (7)	0.0225 (8)	0.0001 (7)
C16	0.0223 (8)	0.0209 (9)	0.0218 (8)	-0.0001 (7)	0.0125 (7)	-0.0009 (7)
N1	0.0182 (7)	0.0218 (8)	0.0182 (7)	-0.0015 (6)	0.0097 (6)	0.0009 (5)
N2	0.0204 (7)	0.0213 (8)	0.0188 (7)	-0.0005 (6)	0.0116 (6)	0.0004 (6)
O1	0.0152 (6)	0.0285 (7)	0.0151 (5)	-0.0033 (5)	0.0065 (5)	0.0033 (5)
O2	0.0162 (6)	0.0306 (7)	0.0185 (6)	-0.0019 (5)	0.0089 (5)	0.0036 (5)

Geometric parameters (Å, °)

C1—O1	1.3301 (18)	C11—C16	1.389 (2)
C1—C2	1.380 (2)	C11—C12	1.395 (2)
C1—C7	1.471 (2)	C11—N2	1.4378 (19)
C2—C3	1.397 (2)	C12—C13	1.385 (2)
C2—H2	0.95	C12—H12	0.95
C3—C4	1.379 (2)	C13—C14	1.389 (2)
C3—H3	0.95	C13—H13	0.95
C4—C5	1.414 (2)	C14—C15	1.383 (2)
C4—N1	1.4342 (19)	C14—H14	0.95
C5—C6	1.362 (2)	C15—C16	1.390 (2)
C5—H5	0.95	C15—H15	0.95
C6—C7	1.429 (2)	C16—H16	0.95
C6—H6	0.95	N1—N2	1.2530 (19)
C7—O2	1.2521 (18)	O1—H1	0.84
O1—C1—C2	116.06 (13)	C16—C11—C12	120.25 (14)
O1—C1—C7	114.31 (13)	C16—C11—N2	116.06 (14)
C2—C1—C7	129.62 (14)	C12—C11—N2	123.69 (14)
C1—C2—C3	130.28 (14)	C13—C12—C11	119.66 (15)
C1—C2—H2	114.9	C13—C12—H12	120.2
C3—C2—H2	114.9	C11—C12—H12	120.2
C4—C3—C2	128.53 (15)	C12—C13—C14	120.16 (16)
C4—C3—H3	115.7	C12—C13—H13	119.9
C2—C3—H3	115.7	C14—C13—H13	119.9
C3—C4—C5	126.89 (14)	C15—C14—C13	120.03 (15)
C3—C4—N1	122.36 (14)	C15—C14—H14	120
C5—C4—N1	110.72 (13)	C13—C14—H14	120
C6—C5—C4	131.02 (15)	C14—C15—C16	120.34 (16)
C6—C5—H5	114.5	C14—C15—H15	119.8
C4—C5—H5	114.5	C16—C15—H15	119.8
C5—C6—C7	130.70 (15)	C11—C16—C15	119.55 (15)
C5—C6—H6	114.7	C11—C16—H16	120.2

C7—C6—H6	114.7	C15—C16—H16	120.2
O2—C7—C6	120.84 (14)	N2—N1—C4	116.00 (13)
O2—C7—C1	116.31 (14)	N1—N2—C11	112.83 (13)
C6—C7—C1	122.85 (14)	C1—O1—H1	109.5
O1—C1—C2—C3	-178.41 (16)	C16—C11—C12—C13	0.0 (2)
C7—C1—C2—C3	2.7 (3)	N2—C11—C12—C13	179.29 (15)
C1—C2—C3—C4	-0.4 (3)	C11—C12—C13—C14	-0.1 (3)
C2—C3—C4—C5	-2.9 (3)	C12—C13—C14—C15	0.0 (3)
C2—C3—C4—N1	179.51 (16)	C13—C14—C15—C16	0.3 (3)
C3—C4—C5—C6	2.2 (3)	C12—C11—C16—C15	0.3 (2)
N1—C4—C5—C6	-179.90 (17)	N2—C11—C16—C15	-179.08 (15)
C4—C5—C6—C7	1.3 (3)	C14—C15—C16—C11	-0.4 (3)
C5—C6—C7—O2	178.42 (17)	C3—C4—N1—N2	-4.4 (2)
C5—C6—C7—C1	-2.1 (3)	C5—C4—N1—N2	177.61 (14)
O1—C1—C7—O2	-0.2 (2)	C4—N1—N2—C11	-179.34 (13)
C2—C1—C7—O2	178.73 (16)	C16—C11—N2—N1	-177.26 (14)
O1—C1—C7—C6	-179.64 (14)	C12—C11—N2—N1	3.4 (2)
C2—C1—C7—C6	-0.7 (3)		

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots O2	0.84	2.08	2.5754 (15)	117
C5—H5 \cdots O1 ⁱ	0.95	2.40	3.1866 (19)	140
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