



Crystal structure of (*E*)-2,6-di-*tert*-butyl-4-[[2-(2,4-dinitrophenyl)hydrazinylidene]methyl]phenol

Md. Serajul Haque Faizi,^a Necmi Dege,^b Ashanul Haque,^a Valentina A. Kalibabchuk^{c*} and Mustafa Cemberci^b

^aDepartment of Chemistry, College of Science, Sultan Qaboos University, PO Box 36, Al-Khod 123, Muscat, Sultanate of Oman, ^bOndokuz Mayıs University, Arts and Sciences Faculty, Department of Physics, 55139 Samsun, Turkey, and ^cDepartment of General Chemistry, O. O. Bohomolets National Medical University, Shevchenko Blvd. 13, 01601 Kiev, Ukraine. *Correspondence e-mail: kalibabchuk@ukr.net

Received 14 December 2016

Accepted 17 December 2016

Edited by H. Stoeckli-Evans, University of Neuchâtel, Switzerland

Keywords: crystal structure; hydrazine; dinitrobenzene; di-*tert*-butylphenol; 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde; 2,4-dinitrophenylhydrazine; hydrogen bonding.

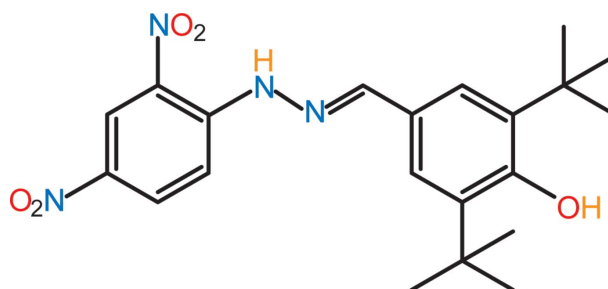
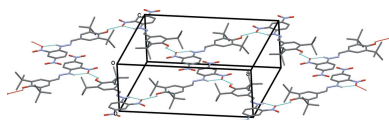
CCDC reference: 1523249

Supporting information: this article has supporting information at journals.iucr.org/e

The essential part (including all the non-hydrogen atoms except two methyl carbons) of the molecule of the title compound, C₂₁H₂₆N₄O₅, lies on a mirror plane, which bisects the *t*-butyl groups. The conformation of the C=N bond of this Schiff base compound is *E*, and there is an intramolecular N—H···O hydrogen bond present, forming an *S*(6) ring motif. In the crystal, molecules are linked *via* O—H···O hydrogen bonds, forming zigzag chains propagating along the *a*-axis direction. There are no other significant intermolecular contacts present.

1. Chemical context

Sterically hindered phenol anti-oxidants are widely used in polymers and lubricants. They can protect polymers by increasing both their process stability and their long-term stability against oxidative degradation (Yamazaki & Seguchi, 1997; Silin *et al.*, 1999). Hydrazones and Schiff bases have attracted much attention for their excellent biological properties, especially for their potential pharmacological and antitumor properties (Küçükgülzel *et al.*, 2006; Khattab, 2005; Karthikeyan *et al.*, 2006; Okabe *et al.*, 1993). 2,4-Dinitrophenylhydrazine is frequently used as a reagent for the characterization of aldehydes and ketones (Furniss *et al.*, 1999). Its derivatives are widely used as dyes (Guillaumont & Nakamura, 2000). They are also found to have versatile coordinating abilities towards different metal ions (Raj & Kurup, 2007). The present work is a part of an ongoing structural study of Schiff bases and their utilization in the synthesis of quinoxaline derivatives (Faizi *et al.*, 2016*a*), fluorescence sensors (Faizi *et al.*, 2016*b*) and coordination compounds (Faizi & Prisyazhnaya, 2015). We report herein on the synthesis and crystal structure of the title Schiff base compound with a sterically hindered phenol group.



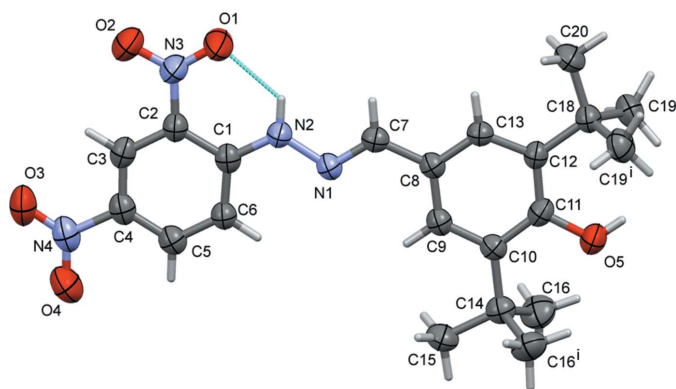


Figure 1
The molecular structure of the title compound, with atom labelling [symmetry code: (i) $x, -y + \frac{1}{2}, z$]. Displacement ellipsoids are drawn at the 30% probability level. The intramolecular N—H \cdots O hydrogen bond is shown as a dashed line (see Table 1)

2. Structural commentary

The molecular structure of the title compound is shown in Fig. 1. All the non-hydrogen atoms except C16 and C19 lie on a crystallographic mirror plane at $y = \frac{1}{4}$; the complete *tert*-butyl groups are generated by mirror symmetry. The conformation of the C7=N1 bond of this Schiff base compound is *E*, and there is an intramolecular N2—H2 \cdots O1 hydrogen bond present, forming an *S*(6) ring motif (Fig. 1 and Table 1). The N1—N2 bond length is 1.385 (6) Å and the N1=C7 bond length is 1.278 (7) Å. The bond distances and angles in the title compound are comparable to those found in a closely related structure (Fun *et al.*, 2013).

3. Supramolecular features

In the crystal, molecules are linked by O—H \cdots O hydrogen bonds, forming zigzag chains propagating along the *a*-axis direction (Fig. 2 and Table 1). There are no other significant intermolecular contacts present.

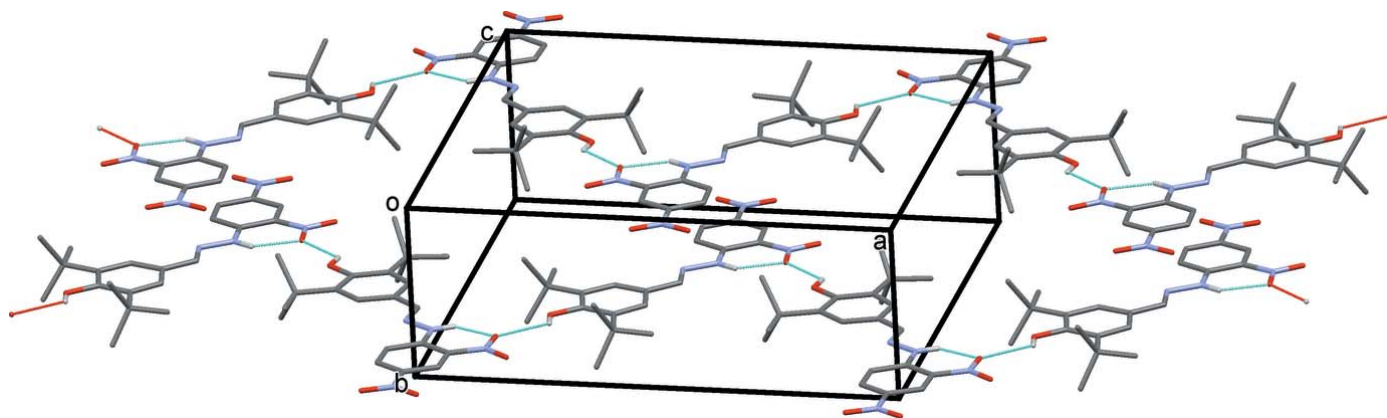


Figure 2
A view of the zigzag chains in the crystal structure of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1). For clarity, only the H atoms involved in hydrogen bonding have been included.

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

<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>
N2—H2 \cdots O1	0.86	1.96	2.583 (8)	129
O5—H5O \cdots O1 ⁱ	0.82 (2)	2.28 (5)	2.782 (7)	120 (4)

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

4. Database survey

There are very few examples of similar compounds in the literature. To the best of our knowledge, the recent report (Bhardwaj & Singh, 2015) of a similar compound with an hydroxy group in the *ortho* position, capable of visual and reversible sensing of cyanide in DMSO solution, has not been characterized crystallographically. A search of the Cambridge Structural Database (CSD, Version 5.37, update May 2016; Groom *et al.*, 2016) revealed the structure of one very similar compound, *viz.* 1-(2,4-dinitrophenyl)-2-[(*E*)-2,4,5-trimethoxybenzylidene]hydrazine (II) (Fun *et al.*, 2013), in which the 4-phenol group in the title compound is replaced by a trimethoxy group. In (II), the dihedral angle between the two benzene rings is 3.15 (11)°, compared to 0° in the title compound, owing to the mirror symmetry.

5. Synthesis and crystallization

A mixture of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde 0.100 g (0.427 mmol) and 2,4-dinitrophenylhydrazine (0.085 g, 0.427 mmol) in methanol was refluxed for 3 h in the presence of a catalytic amount of glacial acetic acid. After cooling, the red-coloured precipitate was washed with hot methanol several times, and then dried, giving a red-coloured shiny crystalline compound in high yield 170 g (96%). Yellow block-like crystals of the title compound (m.p. 372–373 K) were obtained by slow evaporation of a solution in dichloromethane and ethanol (5:1 *v/v*).

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₂₁ H ₂₆ N ₄ O ₅
<i>M</i> _r	414.46
Crystal system, space group	Orthorhombic, <i>Pnma</i>
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	18.7651 (10), 6.9193 (4), 17.259 (1)
<i>V</i> (Å ³)	2240.9 (2)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.22 × 0.15 × 0.11
Data collection	
Diffraction	STOE IPDS 2
Absorption correction	Integration (<i>X-RED32</i> ; Stoe & Cie, 2002)
<i>T</i> _{min} , <i>T</i> _{max}	0.982, 0.994
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	14854, 2270, 912
<i>R</i> _{int}	0.105
(sin θ/λ) _{max} (Å ⁻¹)	0.606
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.071, 0.215, 0.96
No. of reflections	2270
No. of parameters	178
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.39, -0.16

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2002), *SHELXT* (Sheldrick 2015a), *SHELXL2016/4* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2008), *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The OH H atom was located in a difference Fourier map and refined with a distance restraint of 0.82 (2) Å with *U*_{iso}(H) = 1.5*U*_{eq}(O). The NH and C-bound H atoms were included in calculated positions and allowed to ride on the parent atoms: N–H = 0.86 Å, C–H = 0.93–0.96 Å with *U*_{iso}(H) = 1.5*U*_{eq}(C-methyl) and 1.2*U*_{eq}(N,C) for other H atoms.

Acknowledgements

The authors are grateful to Ondokuz Mayıs University, Arts and Sciences Faculty, Department of Physics, Samsun, Turkey, for the X-ray data collection, and Drs Igor Fritsky and Graham Smith for helpful discussions.

References

- Bhardwaj, S. & Singh, A. K. (2015). *J. Hazard. Mater.* **296**, 54–60.
- Faizi, M. S. H., Ali, A. & Potaskalov, V. A. (2016a). *Acta Cryst.* **E72**, 1366–1369.
- Faizi, M. S. H., Gupta, S., Mohan, V. K., Jain, K. V. & Sen, P. (2016b). *Sens. Actuators B Chem.* **222**, 15–20.
- Faizi, M. S. H. & Prisyazhnaya, E. V. (2015). *Acta Cryst.* **E71**, m175–m176.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Fun, H.-K., Chantrapromma, S., Nilwanna, B., Kobkeattawin, T. & Boonnak, N. (2013). *Acta Cryst.* **E69**, o1203–o1204.
- Furniss, B. S., Hannaford, A. J., Smith, P. W. G. & Tatchell, A. R. (1999). *Vogel's Textbook of Practical Organic Chemistry*, 5th ed. London: Longmans.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Guillaumont, D. & Nakamura, S. (2000). *Dyes Pigments*, **46**, 85–92.
- Karthikeyan, M. S., Prasad, D. J., Poojary, B., Bhat, K. S., Holla, B. S. & Kumari, N. S. (2006). *Bioorg. Med. Chem.* **14**, 7482–7489.
- Khattab, S. N. (2005). *Molecules*, **10**, 1218–1228.
- Küçükgülzel, G., Kocatepe, A., De Clercq, E., Şahin, F. & Güllüce, M. (2006). *Eur. J. Med. Chem.* **41**, 353–359.
- Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
- Okabe, N., Nakamura, T. & Fukuda, H. (1993). *Acta Cryst.* **C49**, 1678–1680.
- Raj, B. N. B. & Kurup, M. R. P. (2007). *Spectrochim. Acta Part A*, **66**, 898–903.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Silin, M. A., Kelaren, V. I., Abu-Ammar, V., Putkaradze, D. Kh. & Golubeva, I. A. (1999). *Pet. Chem.* **40**, 209–214.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Stoe & Cie (2002). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.
- Yamazaki, T. & Seguchi, T. (1997). *J. Polym. Sci. A Polym. Chem.* **35**, 2431–2439.

supporting information

Acta Cryst. (2017). E73, 96-98 [https://doi.org/10.1107/S2056989016020107]

Crystal structure of (*E*)-2,6-di-*tert*-butyl-4-[[2-(2,4-dinitrophenyl)hydrazinylidene]methyl]phenol

Md. Serajul Haque Faizi, Necmi Dege, Ashanul Haque, Valentina A. Kalibabchuk and Mustafa Cemberci

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXT* (Sheldrick 2015a); program(s) used to refine structure: *SHELXL2016/4* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *PLATON* (Spek, 2009).

(*E*)-2,6-Di-*tert*-butyl-4-[[2-(2,4-dinitrophenyl)hydrazinylidene]methyl]phenol

Crystal data

$C_{21}H_{26}N_4O_5$

$M_r = 414.46$

Orthorhombic, *Pnma*

$a = 18.7651$ (10) Å

$b = 6.9193$ (4) Å

$c = 17.259$ (1) Å

$V = 2240.9$ (2) Å³

$Z = 4$

$F(000) = 880$

$D_x = 1.228$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6871 reflections

$\theta = 1.1$ – 26.2°

$\mu = 0.09$ mm⁻¹

$T = 296$ K

Block, yellow

$0.22 \times 0.15 \times 0.11$ mm

Data collection

STOE IPDS 2

diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4

mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: integration

(*X-RED32*; Stoe & Cie, 2002)

$T_{\min} = 0.982$, $T_{\max} = 0.994$

14854 measured reflections

2270 independent reflections

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

$R_{\text{int}} = 0.105$

$\theta_{\max} = 25.5^\circ$, $\theta_{\min} = 1.6^\circ$

$h = -22 \rightarrow 22$

$k = -8 \rightarrow 8$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.071$

$wR(F^2) = 0.215$

$S = 0.96$

2270 reflections

178 parameters

2 restraints

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0904P)^2]$

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

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

$$\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$$

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

Special details

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.

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	0.3313 (3)	0.250000	0.5101 (4)	0.172 (3)
O2	0.2860 (3)	0.250000	0.3982 (3)	0.1219 (18)
O3	0.4249 (4)	0.250000	0.1717 (3)	0.1208 (19)
O4	0.5398 (4)	0.250000	0.1781 (3)	0.134 (2)
O5	0.7461 (2)	0.250000	0.8580 (3)	0.0968 (15)
H5O	0.738 (3)	0.250000	0.9045 (15)	0.145*
N1	0.5301 (3)	0.250000	0.5745 (3)	0.0688 (13)
N2	0.4674 (3)	0.250000	0.5319 (3)	0.0755 (14)
H2	0.426908	0.250000	0.555180	0.091*
N3	0.3381 (3)	0.250000	0.4404 (4)	0.0986 (19)
N4	0.4801 (5)	0.250000	0.2079 (4)	0.0960 (18)
C1	0.4705 (4)	0.250000	0.4537 (3)	0.0683 (16)
C2	0.4077 (3)	0.250000	0.4074 (4)	0.0738 (17)
C3	0.4119 (4)	0.250000	0.3273 (4)	0.0743 (17)
H3	0.370779	0.250000	0.297265	0.089*
C4	0.4780 (4)	0.250000	0.2928 (4)	0.0776 (17)
C5	0.5396 (4)	0.250000	0.3361 (4)	0.0778 (18)
H5A	0.583662	0.250000	0.311488	0.093*
C6	0.5360 (3)	0.250000	0.4143 (3)	0.0707 (16)
H6	0.578077	0.250000	0.442879	0.085*
C7	0.5207 (3)	0.250000	0.6478 (4)	0.0686 (16)
H7	0.474375	0.250000	0.666931	0.082*
C8	0.5798 (3)	0.250000	0.7027 (3)	0.0642 (15)
C9	0.6498 (3)	0.250000	0.6776 (3)	0.0677 (15)
H9	0.659076	0.250000	0.624701	0.081*
C10	0.7066 (3)	0.250000	0.7293 (3)	0.0666 (16)
C11	0.6887 (3)	0.250000	0.8089 (4)	0.0739 (17)
C12	0.6187 (3)	0.250000	0.8373 (3)	0.0663 (15)
C13	0.5656 (3)	0.250000	0.7812 (3)	0.0656 (15)
H13	0.518293	0.250000	0.797276	0.079*
C14	0.7841 (3)	0.250000	0.7007 (4)	0.0775 (18)
C15	0.7881 (4)	0.250000	0.6117 (4)	0.098 (2)
H15A	0.764903	0.136762	0.592106	0.146*
H15B	0.837191	0.250000	0.596024	0.146*
C16	0.8233 (2)	0.4334 (8)	0.7297 (3)	0.1114 (18)
H16A	0.797329	0.546218	0.713820	0.167*
H16B	0.870376	0.437202	0.708115	0.167*
H16C	0.826331	0.430459	0.785250	0.167*

C18	0.6013 (3)	0.250000	0.9242 (3)	0.0755 (18)
C19	0.6312 (3)	0.4323 (7)	0.9640 (2)	0.0973 (16)
H19A	0.679150	0.408097	0.980849	0.146*
H19B	0.602137	0.464417	1.007856	0.146*
H19C	0.631039	0.537943	0.927893	0.146*
C20	0.5207 (4)	0.250000	0.9375 (4)	0.102 (2)
H20A	0.500334	0.363387	0.914288	0.154*
H20B	0.511112	0.250000	0.991999	0.154*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.081 (4)	0.362 (10)	0.073 (4)	0.000	0.007 (3)	0.000
O2	0.083 (4)	0.164 (5)	0.118 (4)	0.000	-0.024 (3)	0.000
O3	0.147 (5)	0.135 (5)	0.080 (4)	0.000	-0.034 (4)	0.000
O4	0.147 (5)	0.177 (6)	0.078 (4)	0.000	0.013 (4)	0.000
O5	0.077 (3)	0.136 (4)	0.078 (3)	0.000	-0.017 (3)	0.000
N1	0.072 (3)	0.078 (3)	0.056 (3)	0.000	0.000 (3)	0.000
N2	0.063 (3)	0.103 (4)	0.061 (3)	0.000	-0.005 (3)	0.000
N3	0.068 (4)	0.145 (6)	0.083 (4)	0.000	-0.009 (4)	0.000
N4	0.130 (6)	0.091 (4)	0.068 (4)	0.000	-0.009 (4)	0.000
C1	0.083 (4)	0.059 (4)	0.064 (4)	0.000	-0.008 (4)	0.000
C2	0.078 (5)	0.081 (4)	0.063 (4)	0.000	-0.010 (4)	0.000
C3	0.082 (5)	0.063 (4)	0.078 (5)	0.000	-0.022 (4)	0.000
C4	0.102 (5)	0.066 (4)	0.065 (4)	0.000	-0.007 (4)	0.000
C5	0.086 (5)	0.077 (4)	0.070 (4)	0.000	0.001 (4)	0.000
C6	0.072 (4)	0.079 (4)	0.061 (4)	0.000	-0.004 (3)	0.000
C7	0.067 (4)	0.069 (4)	0.069 (4)	0.000	0.003 (4)	0.000
C8	0.069 (4)	0.066 (4)	0.058 (4)	0.000	0.001 (3)	0.000
C9	0.077 (4)	0.068 (4)	0.058 (3)	0.000	-0.001 (4)	0.000
C10	0.069 (4)	0.068 (4)	0.063 (4)	0.000	0.003 (3)	0.000
C11	0.064 (4)	0.080 (4)	0.078 (4)	0.000	-0.016 (4)	0.000
C12	0.069 (4)	0.070 (4)	0.060 (4)	0.000	-0.011 (3)	0.000
C13	0.061 (4)	0.072 (4)	0.064 (4)	0.000	0.002 (3)	0.000
C14	0.075 (4)	0.076 (4)	0.082 (4)	0.000	0.001 (4)	0.000
C15	0.084 (5)	0.125 (6)	0.084 (5)	0.000	0.019 (4)	0.000
C16	0.086 (3)	0.122 (4)	0.126 (5)	-0.028 (3)	0.000 (3)	0.000 (4)
C18	0.076 (4)	0.090 (5)	0.061 (4)	0.000	-0.004 (3)	0.000
C19	0.115 (4)	0.109 (4)	0.068 (3)	-0.002 (3)	-0.002 (3)	-0.013 (3)
C20	0.089 (5)	0.147 (7)	0.071 (4)	0.000	0.017 (4)	0.000

Geometric parameters (Å, °)

O1—N3	1.209 (7)	C9—H9	0.9300
O2—N3	1.219 (7)	C10—C11	1.415 (8)
O3—N4	1.210 (7)	C10—C14	1.536 (8)
O4—N4	1.232 (8)	C11—C12	1.401 (8)
O5—C11	1.370 (7)	C12—C13	1.390 (8)

O5—H5O	0.816 (19)	C12—C18	1.536 (8)
N1—C7	1.278 (7)	C13—H13	0.9300
N1—N2	1.385 (6)	C14—C15	1.538 (9)
N2—C1	1.352 (7)	C14—C16	1.549 (6)
N2—H2	0.8600	C14—C16 ⁱ	1.549 (6)
N3—C2	1.424 (8)	C15—H15A	0.96
N4—C4	1.466 (8)	C15—H15B	0.96
C1—C6	1.405 (8)	C15—H15A ⁱ	0.96
C1—C2	1.422 (8)	C16—H16A	0.9600
C2—C3	1.385 (8)	C16—H16B	0.9600
C3—C4	1.374 (8)	C16—H16C	0.9600
C3—H3	0.9300	C18—C20	1.530 (9)
C4—C5	1.376 (9)	C18—C19	1.542 (5)
C5—C6	1.352 (8)	C18—C19 ⁱ	1.542 (5)
C5—H5A	0.9300	C19—H19A	0.9600
C6—H6	0.9300	C19—H19B	0.9600
C7—C8	1.458 (8)	C19—H19C	0.9600
C7—H7	0.9300	C20—H20A	0.96
C8—C13	1.380 (7)	C20—H20B	0.96
C8—C9	1.383 (8)	C20—H20A ⁱ	0.96
C9—C10	1.390 (8)		
C11—O5—H5O	118 (4)	C12—C11—C10	124.2 (6)
C7—N1—N2	114.1 (5)	C13—C12—C11	115.4 (5)
C1—N2—N1	119.6 (5)	C13—C12—C18	121.9 (5)
C1—N2—H2	120.2	C11—C12—C18	122.7 (5)
N1—N2—H2	120.2	C8—C13—C12	123.0 (6)
O1—N3—O2	120.6 (6)	C8—C13—H13	118.5
O1—N3—C2	119.7 (6)	C12—C13—H13	118.5
O2—N3—C2	119.7 (6)	C10—C14—C15	111.5 (5)
O3—N4—O4	124.2 (7)	C10—C14—C16	110.2 (3)
O3—N4—C4	119.5 (8)	C15—C14—C16	107.4 (4)
O4—N4—C4	116.3 (7)	C10—C14—C16 ⁱ	110.2 (3)
N2—C1—C6	121.3 (6)	C15—C14—C16 ⁱ	107.4 (4)
N2—C1—C2	121.8 (6)	C16—C14—C16 ⁱ	110.0 (6)
C6—C1—C2	117.0 (5)	C14—C15—H15A	109.3
C3—C2—C1	120.9 (6)	C14—C15—H15B	109.2
C3—C2—N3	116.9 (6)	H15A—C15—H15B	109.6
C1—C2—N3	122.3 (6)	C14—C15—H15A ⁱ	109.3 (4)
C4—C3—C2	118.9 (6)	H15A—C15—H15A ⁱ	109.7
C4—C3—H3	120.5	H15B—C15—H15A ⁱ	109.6
C2—C3—H3	120.5	C14—C16—H16A	109.5
C3—C4—C5	121.5 (6)	C14—C16—H16B	109.5
C3—C4—N4	117.2 (7)	H16A—C16—H16B	109.5
C5—C4—N4	121.3 (7)	C14—C16—H16C	109.5
C6—C5—C4	120.1 (7)	H16A—C16—H16C	109.5
C6—C5—H5A	120.0	H16B—C16—H16C	109.5
C4—C5—H5A	120.0	C20—C18—C12	110.9 (5)

C5—C6—C1	121.7 (6)	C20—C18—C19	107.1 (4)
C5—C6—H6	119.2	C12—C18—C19	110.9 (3)
C1—C6—H6	119.2	C20—C18—C19 ⁱ	107.1 (4)
N1—C7—C8	122.6 (6)	C12—C18—C19 ⁱ	110.9 (3)
N1—C7—H7	118.7	C19—C18—C19 ⁱ	109.8 (5)
C8—C7—H7	118.7	C18—C19—H19A	109.5
C13—C8—C9	119.4 (6)	C18—C19—H19B	109.5
C13—C8—C7	119.4 (6)	H19A—C19—H19B	109.5
C9—C8—C7	121.2 (5)	C18—C19—H19C	109.5
C8—C9—C10	121.8 (6)	H19A—C19—H19C	109.5
C8—C9—H9	119.1	H19B—C19—H19C	109.5
C10—C9—H9	119.1	C18—C20—H20A	109.3
C9—C10—C11	116.2 (6)	C18—C20—H20B	109.5
C9—C10—C14	121.4 (5)	H20A—C20—H20B	109.6
C11—C10—C14	122.4 (5)	C18—C20—H20A ⁱ	109.3 (5)
O5—C11—C12	121.4 (6)	H20A—C20—H20A ⁱ	109.6
O5—C11—C10	114.4 (6)	H20B—C20—H20A ⁱ	109.6
C7—N1—N2—C1	180.000 (1)	C7—C8—C9—C10	180.000 (1)
N1—N2—C1—C6	0.000 (1)	C8—C9—C10—C11	0.000 (2)
N1—N2—C1—C2	180.000 (1)	C8—C9—C10—C14	180.000 (1)
N2—C1—C2—C3	180.000 (1)	C9—C10—C11—O5	180.000 (1)
C6—C1—C2—C3	0.000 (1)	C14—C10—C11—O5	0.000 (1)
N2—C1—C2—N3	0.000 (1)	C9—C10—C11—C12	0.000 (2)
C6—C1—C2—N3	180.000 (1)	C14—C10—C11—C12	180.000 (1)
O1—N3—C2—C3	180.000 (1)	O5—C11—C12—C13	180.000 (1)
O2—N3—C2—C3	0.000 (1)	C10—C11—C12—C13	0.000 (2)
O1—N3—C2—C1	0.000 (1)	O5—C11—C12—C18	0.000 (2)
O2—N3—C2—C1	180.000 (1)	C10—C11—C12—C18	180.000 (2)
C1—C2—C3—C4	0.000 (1)	C9—C8—C13—C12	0.000 (2)
N3—C2—C3—C4	180.000 (1)	C7—C8—C13—C12	180.000 (1)
C2—C3—C4—C5	0.000 (1)	C11—C12—C13—C8	0.000 (2)
C2—C3—C4—N4	180.000 (1)	C18—C12—C13—C8	180.000 (2)
O3—N4—C4—C3	0.000 (1)	C9—C10—C14—C15	0.000 (2)
O4—N4—C4—C3	180.000 (1)	C11—C10—C14—C15	180.000 (1)
O3—N4—C4—C5	180.000 (1)	C9—C10—C14—C16	119.2 (4)
O4—N4—C4—C5	0.000 (1)	C11—C10—C14—C16	-60.8 (4)
C3—C4—C5—C6	0.000 (1)	C9—C10—C14—C16 ⁱ	-119.2 (4)
N4—C4—C5—C6	180.000 (1)	C11—C10—C14—C16 ⁱ	60.8 (4)
C4—C5—C6—C1	0.000 (1)	C13—C12—C18—C20	0.000 (2)
N2—C1—C6—C5	180.000 (1)	C11—C12—C18—C20	180.000 (2)
C2—C1—C6—C5	0.000 (1)	C13—C12—C18—C19	-118.8 (4)
N2—N1—C7—C8	180.000 (1)	C11—C12—C18—C19	61.2 (4)
N1—C7—C8—C13	180.000 (1)	C13—C12—C18—C19 ⁱ	118.8 (4)
N1—C7—C8—C9	0.000 (2)	C11—C12—C18—C19 ⁱ	-61.2 (4)
C13—C8—C9—C10	0.000 (2)		

Symmetry code: (i) $x, -y+1/2, z$.

Hydrogen-bond geometry (Å, °)

<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>
N2—H2 \cdots O1	0.86	1.96	2.583 (8)	129
O5—H5O \cdots O1 ⁱⁱ	0.82 (2)	2.28 (5)	2.782 (7)	120 (4)

Symmetry code: (ii) $x+1/2, y, -z+3/2$.