organic compounds

5-(3,4-Dimethoxybenzylidene)-1,3-dimethyl-1,3-diazinane-2,4,6-trione

Mukut Gohain, Theunis J. Muller* and Barend C. B. Bezuidenhoudt

Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein 9300, South Africa

Correspondence e-mail: muller.theunis@gmail.com

In the title compound, $C_{15}H_{16}N_2O_5$, the dihedral angle between 1,3-diazinane and benzene rings is only 4.27 (1)°. The essentially planar molecular structure is characterized by a short intramolecular C—H⋯O separation and by an exceptionally large bond angle of 138.25 (14)° at the bridging methine C atom. The methoxy groups deviate somewhat from the plane of the benzene ring, with C—C—O—C torsion angles of −15.6 (1) and 9.17 (6)°. In the crystal, molecules form centrosymmetric dimers via donor–acceptor π–π interactions, with a centroid–centroid distance of 3.401 (1) Å.

Related literature

For the biological activity of 1,3-diazinane derivatives, see: Negwar (2001); Tanaka *et al.* (1986, 1988). For the use of pyridine-type ligands in catalysis models, see: Roodt *et al.* (2011); van der Westhuizen *et al.* (2010). For related structures, see: Panchatcharam *et al.* (2009); Rezende *et al.* (2005). For the synthesis, see: Prajapati *et al.* (2006). For standard bond lengths, see: Allen *et al.* (1987).
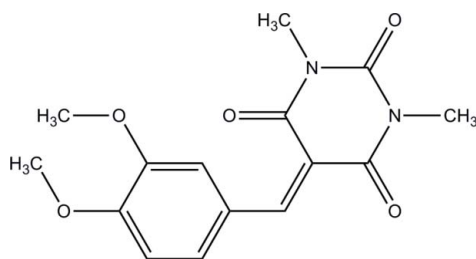
Experimental

Crystal data

$C_{15}H_{16}N_2O_5$
M_r = 304.3
Triclinic, $P\bar{1}$
a = 7.3086 (2) Å
b = 8.4033 (3) Å
c = 11.8705 (5) Å
α = 82.5685 (18)°
β = 77.6686 (17)°
γ = 71.1469 (15)°
V = 672.58 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 100 K
$0.15 \times 0.12 \times 0.06$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.984, T_{max} = 0.994
12172 measured reflections
3233 independent reflections
2478 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.113
S = 1.05
3233 reflections
203 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C7—H7⋯O3	0.93	2.08	2.871 (2)	142

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); 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* (Brandenberg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Brandenberg, K. & Putz, H. (2005). *DIAMOND*. Crystal Impact, Bonn, Germany.
Bruker (2008). *APEX2*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Negwar, M. (2001). *Organic–Chemical Drugs and their Synonyms*, 7th Rev. and Engl. ed., Vol. 4, pp. 2873–2957. Berlin: Akademie.
Panchatcharam, R., Dhayalan, V., Mohanakrishnan, A. K., Chakkaravarthi, G. & Manivannan, V. (2009). *Acta Cryst.* E**65**, o2394.
Prajapati, D. & Gohain, M. (2006). *Beilstein J. Org. Chem.* **2**, No. 11, doi:10.1186/1860-5397-2-11.
Rezende, M. C., Dominguez, M., Wardell, J. L., Skakle, J. M. S., Low, J. N. & Glidewell, C. (2005). *Acta Cryst.* C**61**, o306–o311.
Roodt, A., Visser, H. G. & Brink, A. (2011). *Crystallogr. Rev.* **66**, 241–280.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tanaka, K., Chen, X., Kimura, T. & Yoneda, F. (1986). *Chem. Pharm. Bull.* **34**, 3945–3948.
Tanaka, K., Chen, X., Kimura, T. & Yoneda, F. (1988). *Chem. Pharm. Bull.* **36**, 66–69.
Westhuizen, H. J. van der, Meijboom, R., Schutte, M. & Roodt, A. (2010). *Inorg. Chem.* **49**, 9599–9608.

supporting information

5-(3,4-Dimethoxybenzylidene)-1,3-dimethyl-1,3-diazinane-2,4,6-trione

Mukut Gohain, Theunis J. Muller and Barend C. B. Bezuidenhoudt

S1. Comment

Barbituric acid is the parent compound of barbiturate drugs, although by itself it is not pharmacologically active (Negwar *et al.*, 2001). Benzyledenebarbituric acids are important building block in the synthesis of pyrazolo-[3,4]-1,3-diazinane derivatives which shows broad-spectrum biological activities (Tanaka *et al.*, 1986 and 1988). We also synthesized some of the benzyledene barbituric acids which were successfully used to prepare pyrano[2,3-*d*]- and furopyrano[2,3-*d*] 1,3-diazinane derivatives (Prajapati *et al.*, 2006). The title compound having molecular formula $C_{15}H_{16}N_2O_5$ can be prepared by the condensation of barbituric acid and 4,5-dimethoxybenzaldehyde. The bond C5—C6 of 1.453 (2) Å is longer than C3—C5 bond of 1.365 (2) Å that indicates C3—C5 as a formally double bond. This is in accordance with the literature (Panchatcharam *et al.* 2009 and Rezende *et al.* 2005).

S2. Experimental

Mixture of *N,N*-dimethylbarbituric acid (0.50 g, 3.2 mmol) and 4,5-dimethoxy benzaldehyde (0.53 g, 3.2 mmol) in ethanol (10 ml) was stirred at room temperature until completion of the reaction (monitored by TLC). The solids that precipitated during the course of the reaction were filtered and washed with diethyl ether (5 ml). The precipitate was subsequently dissolved in hot acetonitrile. Upon cooling to room temperature with a slow evaporation of the acetonitrile the crystals (mp 229–230 °C) suitable for single-crystal X-ray diffraction were obtained.

^{1}H NMR (600 MHz): 3.42 (s, 3H, N—Me), 3.43 (s, 3H, N—Me), 3.99 (s, 3H, OMe), 3.40 (s, 3H, OMe), 6.97 (d, 1H), 7.81 (dd, 1H), 8.41 (d, 1H), 8.51(s, 1H).

^{13}C {^{1}H} NMR (150Mz): 28.5, 29.1, 56.1, 56.2, 110.4, 114.2, 116.6, 125.9, 132.6, 148.4, 151.4, 154.4, 159.2, 161.1, 163.3.

S3. Refinement

The aromatic H atoms were positioned geometrically and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}$(parent) of the parent atom with a C—H distance of 0.93. The methyl H atoms were placed in geometrically idealized positions and constrained to ride on its parent atoms with $U_{iso}(H) = 1.5U_{eq}(C)$ and at a distance of 0.96 Å; their torsion angles were optimized from electron density
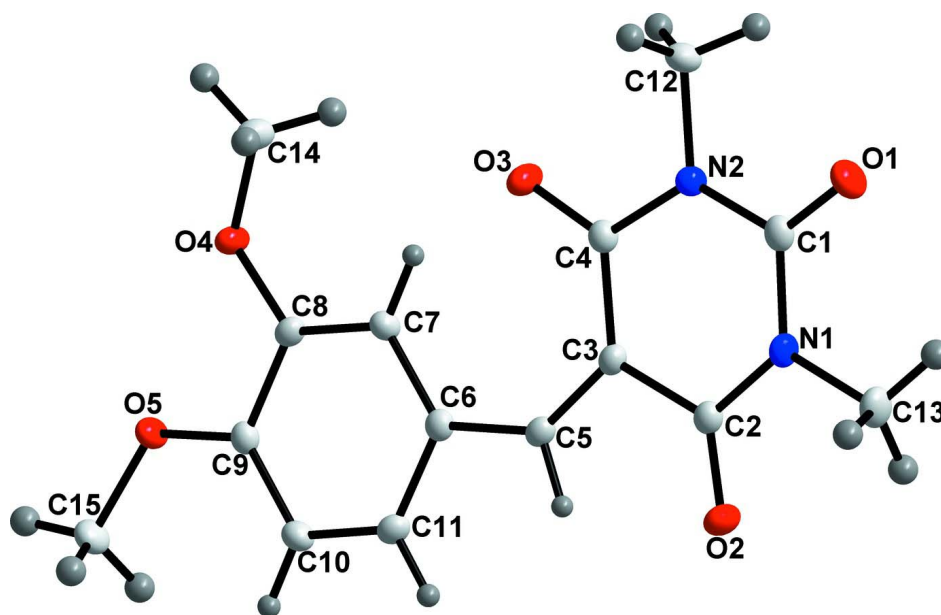
Figure 1

Diamond representation of the title compound, showing the numbering scheme and displacement ellipsoids (50% probability).
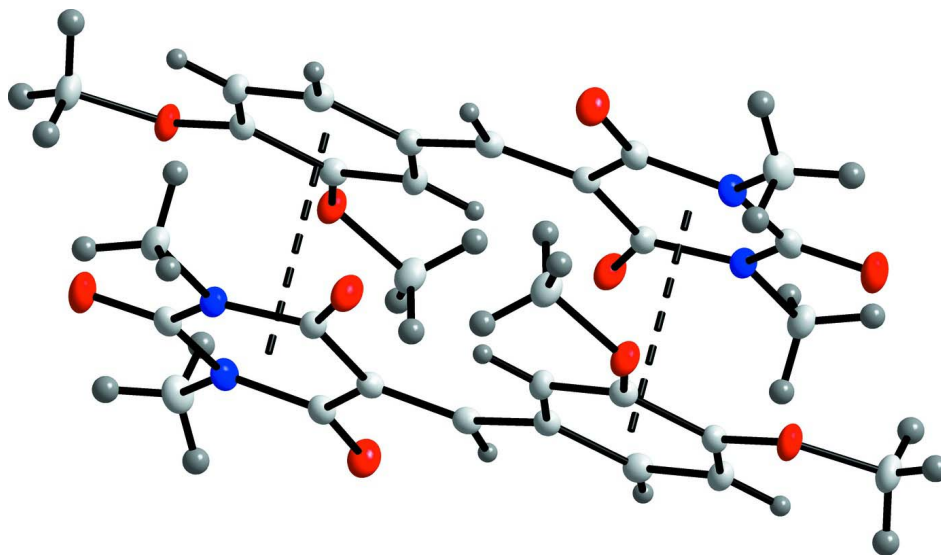
Figure 2

Diamond representation of the title compound, showing the π-π interaction.

5-(3,4-Dimethoxybenzylidene)-1,3-dimethyl-1,3-diazinane-2,4,6-trione

Crystal data

$C_{15}H_{16}N_2O_5$	$b = 8.4033$ (3) Å
$M_r = 304.3$	$c = 11.8705$ (5) Å
Triclinic, $P\bar{1}$	$\alpha = 82.5685$ (18)°
Hall symbol: -P 1	$\beta = 77.6686$ (17)°
$a = 7.3086$ (2) Å	$\gamma = 71.1469$ (15)°

$V = 672.58$ (4) Å^3

$Z = 2$

$F(000) = 320$

$D_x = 1.508$ Mg m^{-3}

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

Cell parameters from 3146 reflections

$\theta = 2.6–28.2°$

$\mu = 0.11$ mm^{-1}

$T = 100$ K

Plate, yellow

$0.15 \times 0.12 \times 0.06$ mm

Data collection

Bruker APEXII CCD diffractometer

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2008)

$T_{min} = 0.984$, $T_{max} = 0.994$

12172 measured reflections

3233 independent reflections

2478 reflections with $I > 2\sigma(I)$

$R_{int} = 0.032$

$\theta_{max} = 28°$, $\theta_{min} = 3.2°$

$h = -9 \rightarrow 9$

$k = -11 \rightarrow 11$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.113$

$S = 1.05$

3233 reflections

203 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.239P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.32$ e Å^{-3}

$\Delta\rho_{min} = -0.30$ e Å^{-3}

Special details

Experimental. The intensity data was collected on a Bruker X8 ApexII 4 K Kappa CCD diffractometer using an exposure time of 15 s/frame. A total of 1821 frames were collected with a frame width of 0.5° covering up to $\theta = 28.18°$ with 99.7% completeness accomplished.

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.4027 (2)	0.72599 (19)	0.80997 (12)	0.0160 (3)
C2	0.5148 (2)	0.43533 (18)	0.75097 (12)	0.0150 (3)
C3	0.61438 (19)	0.49161 (18)	0.63713 (12)	0.0135 (3)
C4	0.59797 (19)	0.67081 (18)	0.61360 (12)	0.0144 (3)
C5	0.70824 (19)	0.36478 (18)	0.56448 (12)	0.0139 (3)
H5	0.6895	0.2635	0.5979	0.017*
C6	0.82904 (19)	0.34247 (18)	0.44990 (12)	0.0138 (3)
C7	0.89371 (19)	0.46673 (18)	0.37541 (12)	0.0142 (3)

H7	0.8572	0.576	0.3985	0.017*
C8	1.01025 (19)	0.42763 (18)	0.26903 (12)	0.0138 (3)
C9	1.06655 (19)	0.26239 (18)	0.23180 (12)	0.0142 (3)
C10	1.0028 (2)	0.13956 (18)	0.30414 (12)	0.0160 (3)
H10	1.0382	0.0306	0.2807	0.019*
C11	0.8865 (2)	0.17974 (18)	0.41127 (12)	0.0155 (3)
H11	0.8452	0.0963	0.459	0.019*
C12	0.4873 (2)	0.95348 (18)	0.68221 (13)	0.0186 (3)
H12A	0.3864	1.0081	0.6375	0.028*
H12B	0.6109	0.9644	0.6403	0.028*
H12C	0.4551	1.0052	0.7544	0.028*
C13	0.3059 (2)	0.5045 (2)	0.93915 (13)	0.0215 (3)
H13A	0.2832	0.5852	0.9949	0.032*
H13B	0.3826	0.396	0.9664	0.032*
H13C	0.1822	0.498	0.9283	0.032*
C14	0.9864 (2)	0.71432 (18)	0.21141 (14)	0.0203 (3)
H14A	0.8468	0.7402	0.2177	0.03*
H14B	1.0356	0.7815	0.1479	0.03*
H14C	1.0144	0.7384	0.2817	0.03*
C15	1.2176 (2)	0.08217 (19)	0.07552 (14)	0.0215 (3)
H15A	1.29	−0.0087	0.122	0.032*
H15B	1.2928	0.0848	−0.0012	0.032*
H15C	1.0949	0.0657	0.0724	0.032*
N1	0.41279 (17)	0.55732 (16)	0.82856 (10)	0.0161 (3)
N2	0.50181 (17)	0.77434 (15)	0.70439 (10)	0.0151 (3)
O5	1.18050 (15)	0.23929 (13)	0.12565 (9)	0.0181 (2)
O1	0.31031 (16)	0.82697 (14)	0.88192 (9)	0.0229 (3)
O2	0.51855 (15)	0.28912 (13)	0.77753 (9)	0.0216 (3)
O3	0.66023 (15)	0.73491 (13)	0.52101 (9)	0.0210 (3)
O4	1.07951 (14)	0.53932 (13)	0.19183 (9)	0.0174 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0140 (6)	0.0205 (8)	0.0140 (7)	−0.0057 (6)	−0.0022 (5)	−0.0026 (6)
C2	0.0151 (6)	0.0175 (7)	0.0130 (7)	−0.0061 (6)	−0.0020 (5)	−0.0008 (6)
C3	0.0134 (6)	0.0152 (7)	0.0116 (7)	−0.0049 (5)	−0.0022 (5)	0.0006 (5)
C4	0.0129 (6)	0.0161 (7)	0.0135 (7)	−0.0035 (5)	−0.0013 (5)	−0.0022 (6)
C5	0.0138 (6)	0.0149 (7)	0.0135 (7)	−0.0058 (5)	−0.0027 (5)	0.0013 (6)
C6	0.0128 (6)	0.0156 (7)	0.0128 (7)	−0.0041 (5)	−0.0024 (5)	−0.0010 (5)
C7	0.0148 (6)	0.0137 (7)	0.0141 (7)	−0.0048 (5)	−0.0006 (5)	−0.0028 (5)
C8	0.0136 (6)	0.0147 (7)	0.0134 (7)	−0.0061 (5)	−0.0014 (5)	0.0009 (5)
C9	0.0134 (6)	0.0164 (7)	0.0124 (7)	−0.0042 (5)	−0.0015 (5)	−0.0023 (6)
C10	0.0172 (7)	0.0137 (7)	0.0167 (7)	−0.0040 (5)	−0.0024 (5)	−0.0032 (6)
C11	0.0161 (6)	0.0151 (7)	0.0160 (7)	−0.0070 (6)	−0.0023 (5)	0.0012 (6)
C12	0.0216 (7)	0.0140 (7)	0.0201 (8)	−0.0058 (6)	−0.0013 (6)	−0.0034 (6)
C13	0.0228 (8)	0.0279 (9)	0.0138 (8)	−0.0110 (7)	0.0020 (6)	−0.0015 (6)
C14	0.0237 (7)	0.0153 (8)	0.0203 (8)	−0.0067 (6)	0.0005 (6)	−0.0010 (6)

C15	0.0267 (8)	0.0176 (8)	0.0184 (8)	−0.0053 (6)	0.0009 (6)	−0.0067 (6)
N1	0.0171 (6)	0.0192 (7)	0.0118 (6)	−0.0075 (5)	0.0008 (5)	−0.0008 (5)
N2	0.0164 (6)	0.0144 (6)	0.0143 (6)	−0.0055 (5)	−0.0007 (5)	−0.0013 (5)
O5	0.0226 (5)	0.0156 (5)	0.0142 (5)	−0.0063 (4)	0.0041 (4)	−0.0049 (4)
O1	0.0253 (6)	0.0234 (6)	0.0184 (6)	−0.0077 (5)	0.0040 (4)	−0.0085 (5)
O2	0.0284 (6)	0.0173 (6)	0.0177 (6)	−0.0099 (5)	0.0016 (4)	0.0015 (4)
O3	0.0271 (6)	0.0154 (5)	0.0160 (6)	−0.0056 (4)	0.0031 (4)	0.0008 (4)
O4	0.0214 (5)	0.0133 (5)	0.0154 (5)	−0.0067 (4)	0.0033 (4)	−0.0008 (4)

Geometric parameters (Å, º)

C1—O1	1.2150 (18)	C10—C11	1.385 (2)
C1—N1	1.386 (2)	C10—H10	0.93
C1—N2	1.3897 (19)	C11—H11	0.93
C2—O2	1.2212 (19)	C12—N2	1.467 (2)
C2—N1	1.3826 (19)	C12—H12A	0.96
C2—C3	1.489 (2)	C12—H12B	0.96
C3—C5	1.365 (2)	C12—H12C	0.96
C3—C4	1.466 (2)	C13—N1	1.4716 (19)
C4—O3	1.2235 (17)	C13—H13A	0.96
C4—N2	1.3914 (19)	C13—H13B	0.96
C5—C6	1.453 (2)	C13—H13C	0.96
C5—H5	0.93	C14—O4	1.4331 (19)
C6—C11	1.402 (2)	C14—H14A	0.96
C6—C7	1.413 (2)	C14—H14B	0.96
C7—C8	1.377 (2)	C14—H14C	0.96
C7—H7	0.93	C15—O5	1.4400 (19)
C8—O4	1.3650 (18)	C15—H15A	0.96
C8—C9	1.416 (2)	C15—H15B	0.96
C9—O5	1.3525 (17)	C15—H15C	0.96
C9—C10	1.389 (2)		
O1—C1—N1	121.71 (14)	N2—C12—H12A	109.5
O1—C1—N2	121.60 (14)	N2—C12—H12B	109.5
N1—C1—N2	116.69 (12)	H12A—C12—H12B	109.5
O2—C2—N1	119.59 (13)	N2—C12—H12C	109.5
O2—C2—C3	123.24 (13)	H12A—C12—H12C	109.5
N1—C2—C3	117.16 (13)	H12B—C12—H12C	109.5
C5—C3—C4	127.56 (13)	N1—C13—H13A	109.5
C5—C3—C2	113.69 (13)	N1—C13—H13B	109.5
C4—C3—C2	118.73 (12)	H13A—C13—H13B	109.5
O3—C4—N2	118.37 (14)	N1—C13—H13C	109.5
O3—C4—C3	125.11 (13)	H13A—C13—H13C	109.5
N2—C4—C3	116.51 (13)	H13B—C13—H13C	109.5
C3—C5—C6	138.25 (14)	O4—C14—H14A	109.5
C3—C5—H5	110.9	O4—C14—H14B	109.5
C6—C5—H5	110.9	H14A—C14—H14B	109.5
C11—C6—C7	117.75 (13)	O4—C14—H14C	109.5

C11—C6—C5	115.55 (13)	H14A—C14—H14C	109.5
C7—C6—C5	126.71 (13)	H14B—C14—H14C	109.5
C8—C7—C6	120.66 (13)	O5—C15—H15A	109.5
C8—C7—H7	119.7	O5—C15—H15B	109.5
C6—C7—H7	119.7	H15A—C15—H15B	109.5
O4—C8—C7	124.60 (13)	O5—C15—H15C	109.5
O4—C8—C9	114.77 (12)	H15A—C15—H15C	109.5
C7—C8—C9	120.64 (13)	H15B—C15—H15C	109.5
O5—C9—C10	125.58 (13)	C2—N1—C1	124.99 (13)
O5—C9—C8	115.28 (12)	C2—N1—C13	117.62 (13)
C10—C9—C8	119.14 (13)	C1—N1—C13	117.39 (12)
C11—C10—C9	119.85 (14)	C1—N2—C4	125.56 (13)
C11—C10—H10	120.1	C1—N2—C12	117.23 (12)
C9—C10—H10	120.1	C4—N2—C12	116.91 (12)
C10—C11—C6	121.96 (13)	C9—O5—C15	117.89 (11)
C10—C11—H11	119	C8—O4—C14	116.37 (11)
C6—C11—H11	119		

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C7—H7⋯O3	0.93	2.08	2.871 (2)	142