

CRYSTALLOGRAPHIC
COMMUNICATIONS

ISSN 2056-9890

Crystal structure of the di-Mannich base 4,4'-dichloro-3,3',5,5'-tetramethyl-2,2'-[imidazoli- dine-1,3-diylbis(methylene)]diphenol

Augusto Rivera,^{a*} Luz Stella Nerio^a and Michael Bolte^b

Received 29 January 2015

Accepted 2 February 2015

Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; imidazolidine; di-Mannich base; hydrogen bonding; *syn* conformation

CCDC reference: 1046907

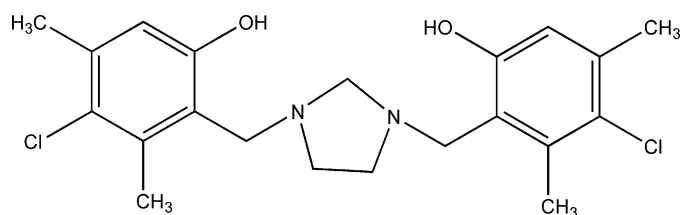
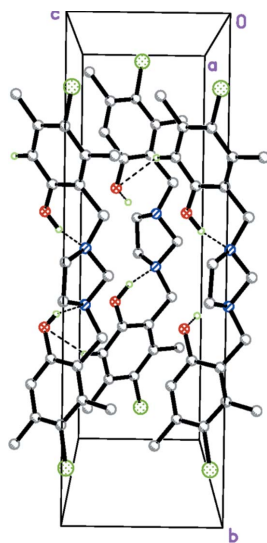
Supporting information: this article has supporting information at journals.iucr.org/e

^aDepartamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Sede Bogotá, Cra 30 No. 45-03, Bogotá, Colombia, and ^bInstitut für Anorganische Chemie, Goethe-Universität, Max-von-Laue-Strasse 7, Frankfurt/Main D-60438, Germany. *Correspondence e-mail: ariverau@unal.edu.co

The title compound, C₂₁H₂₆Cl₂N₂O₂, was prepared in a solvent-free microwave-assisted synthesis, and crystallizes in the orthorhombic space group *Pna*2₁. The imidazolidine ring adopts an envelope conformation and its mean plane is almost perpendicular to the two pendant aromatic rings [dihedral angles = 84.61 (9) and 86.54 (9)°]. The molecular structure shows the presence of two intramolecular O—H···N hydrogen bonds between the phenolic hydroxy groups and imidazolidine N atoms. The two 3-chloro-6-hydroxy-2,4-dimethylbenzyl groups are located in a *cis* orientation with respect to the imidazolidine fragment. As a result, the lone pairs of electrons on the N atoms are presumed to be disposed in a *syn* conformation. This is therefore the first example of an exception to the ‘rabbit-ears’ effect in such 2,2'-[imidazolidine-1,3-diylbis(methylene)]diphenol derivatives.

1. Chemical context

As a continuation of our investigations of the Mannich reaction, we have synthesized a family of compounds of the type 2,2'-[imidazolidine-1,3-diylbis(methylene)]di(hydroxyaryl), from reactions between 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD) and phenols or naphthols (Rivera *et al.*, 1993, 2005; Rivera & Quevedo, 2013). Such compounds are known to be valuable in homogeneous catalysis (Kober *et al.*, 2012) and for the preparation of tetrahydrosalens (Rivera *et al.*, 2004) and heterocalixarenes (Rivera & Quevedo, 2004). Mannich bases are also convenient models for studying the nature of hydrogen bonding and other weak non-covalent interactions, as they contain at least one phenolic or naphtholic hydroxy group as a proton donor, as well as an *ortho*-aminomethyl group as a proton acceptor in the same molecule (Koll *et al.*, 2006). Herein, as part of our systematic investigations of di-Mannich bases as convenient model systems for the study of intramolecular proton-transfer processes, we report the molecular and crystal structure of the title di-Mannich base, 4,4'-dichloro-3,3',5,5'-tetramethyl-2,2'-[imidazolidine-1,3-diylbis(methylene)]diphenol (I).



In a previous report (Rivera & Quevedo, 2013), the title compound (I) was obtained under solvent-free conditions by

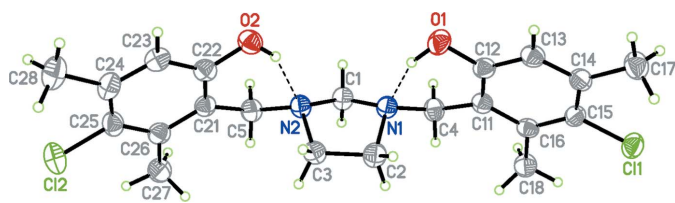


Figure 1

The title molecule, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

heating a 1:4 mixture of TATD and 4-chloro-3,5-dimethylphenol in an oil bath with stirring at 423 K for 20 min. Drawbacks of this synthesis include the long reaction time and a requirement of considerable effort to optimize the reaction conditions and temperature control. We therefore subsequently explored this reaction under solvent-free, microwave-assisted conditions. The reaction was found to proceed smoothly under microwave irradiation in only 3 min at 403 K, in modest yield.

2. Structural commentary

In the title molecule (I), Fig. 1, the imidazolidine ring adopts an envelope conformation, with atom C1 at the flap. The molecular structure shows two intramolecular O—H···N

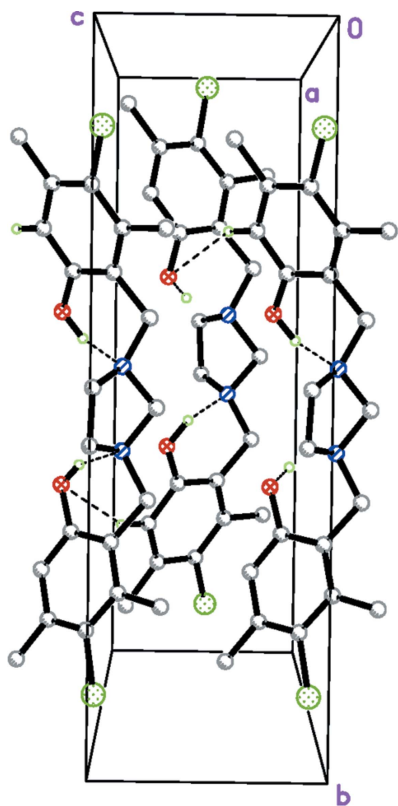


Figure 2

A perspective view along the *a* axis of the crystal packing of the title compound. The C—H···O hydrogen bonds are shown as dashed lines.

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1···N1	0.99 (5)	1.66 (5)	2.606 (3)	158 (4)
O2—H2···N2	0.86 (4)	1.83 (4)	2.619 (3)	152 (3)
C13—H13···O2 ⁱ	0.95	2.59	3.464 (4)	152

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

hydrogen bonds (Table 1) with *S*(6) graph-set motifs between the hydroxy groups of the substituted phenol rings and the two imidazolidine N atoms. The benzyl groups are located in an unexpected 1,3-diequatorial *syn* arrangement on the heterocyclic ring with dihedral angles between the mean plane through the N1/C2/C3/N2 atoms of the imidazolidine ring and the C11—C16 and C21—C26 aromatic rings of 84.61 (9) and 88.54 (9)°, respectively. The non-bonding electron pairs on the imidazolidine N atoms that are involved in both intra- and intermolecular hydrogen-bonding interactions adopt an unusual *syn* arrangement. As such, this molecule defies the well known ‘rabbit-ears’ effect (Hutchins *et al.*, 1968) in which N—CH₂—N systems adopt *anti* conformations to avoid repulsions between the nitrogen lone pairs. Although in the very similar structure of *meso*-4,4′-difluoro-2,2′-[[*(3aR,7aS)*-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3-benzimidazole-1,3-diyl]bis(methylene)]diphenol (Rivera *et al.*, 2013) the N-atom lone pairs are *syn*, molecule (I) is the first reported exception to the ‘rabbit-ears’ effect in compounds of the 2,2′-[imidazolidine-1,3-diylbis(methylene)]diphenol type (Rivera *et al.*, 2011, 2012*a,b,c*, 2013, 2014).

3. Supramolecular features

With both hydroxy groups of (I) involved in intramolecular hydrogen bonds, the only directional interaction in the crystal is a C13—H13···O2ⁱ bond (Table 1 and Fig. 2), which links adjacent molecules in a head-to-tail fashion into zigzag chains, extending along the *c*-axis direction (Fig. 2).

4. Database survey

A search in the Cambridge Structural Database (Groom & Allen 2014) revealed previous reports of six structures of related 2,2′-[imidazolidine-1,3-diylbis(methylene)]diphenol compounds (Rivera *et al.*, 2011, 2012*a,b,c*, 2013, 2014). Each of these also shows intramolecular O—H···N hydrogen bonds between the two imidazolidine N atoms and the hydroxy groups. In addition, the *D*···*A* distances in these compounds compare well with those observed in the title compound. As with (I), the imidazolidine ring in the *p*-*tert*-butylphenol derivative (Rivera *et al.*, 2013), adopts an envelope conformation whereas, in the other five the ring adopts a twist conformation. Furthermore, unlike the title compound, the nitrogen lone pairs in all six of the related derivatives are oriented in an *anti* disposition.

5. Synthesis and crystallization

A mixture of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (0.100 g, 0.6 mmol) and 4-chloro-3,5-dimethylphenol (0.375 g, 2.4 mmol) without any solvent was exposed to microwave irradiation in a CEM Discover reactor (with 250 W as the maximum power) for 3 min at a temperature of 403 K. Once cooled to room temperature, the reaction mixture was dissolved with CHCl₃ which was removed under reduced pressure to yield the crude product. This was further purified by column chromatography on silica gel using a mixture of benzene:ethyl acetate (80:20) as eluent (yield 21%, m.p. = 421–422 K). Single crystals in the form of needles shorter than 1 mm were obtained from a chloroform:ethanol (50:50) solution by slow evaporation of the solvent at room temperature over a period of one week.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the H atoms were located in difference electron density maps. The hydroxy H atoms were freely refined. C-bound H atoms were fixed geometrically (C–H = 0.95 to 0.99 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}$ ($1.5U_{\text{eq}}$ for methyl groups) of the parent atoms. The methyl groups were allowed to rotate but not to tip.

Acknowledgements

We acknowledge the Dirección de Investigaciones, Sede Bogotá (DIB) de la Universidad Nacional de Colombia, for financial support of this work. LSN acknowledges COLCIENCIAS for a fellowship.

References

- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Hutchins, R. O., Kopp, L. D. & Eliel, E. L. (1968). *J. Am. Chem. Soc.* **90**, 7174–7175.
- Kober, E., Nerkowski, T., Janas, Z. & Jerzykiewicz, L. B. (2012). *Dalton Trans.* **41**, 5188–5191.
- Koll, A., Karpfen, A. & Wolschann, P. (2006). *J. Mol. Struct.* **790**, 55–64.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Rivera, A., Gallo, G. I., Gayón, M. E. & Joseph-Nathan, P. (1993). *Synth. Commun.* **23**, 2921–2929.
- Rivera, A., Nerio, L. S. & Bolte, M. (2013). *Acta Cryst.* **E69**, o1166.
- Rivera, A., Nerio, L. S. & Bolte, M. (2014). *Acta Cryst.* **E70**, o243.
- Rivera, A., Nerio, L. S., Ríos-Motta, J., Fejfarová, K. & Dušek, M. (2012a). *Acta Cryst.* **E68**, o170–o171.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₂₁ H ₂₆ Cl ₂ N ₂ O ₂
M_r	409.34
Crystal system, space group	Orthorhombic, <i>Pna</i> 2 ₁
Temperature (K)	173
a, b, c (Å)	20.1594 (11), 17.8088 (12), 5.6120 (3)
V (Å ³)	2014.8 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.34
Crystal size (mm)	0.22 × 0.11 × 0.09
Data collection	
Diffractometer	Stoe <i>IPDS</i> II two circle
Absorption correction	Multi-scan (<i>X-AREA</i> ; Stoe & Cie, 2001)
$T_{\text{min}}, T_{\text{max}}$	0.891, 0.946
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17730, 3708, 3280
R_{int}	0.080
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.604
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.082, 1.00
No. of reflections	3708
No. of parameters	256
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.16, -0.20
Absolute structure	Flack x determined using 1338 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.00 (4)

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2001), *SHELXS87* and *XP* in *SHELXTL-Plus* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015).

- Rivera, A., Nerio, L. S., Ríos-Motta, J., Kučeráková, M. & Dušek, M. (2012b). *Acta Cryst.* **E68**, o3043–o3044.
- Rivera, A., Nerio, L. S., Ríos-Motta, J., Kučeráková, M. & Dušek, M. (2012c). *Acta Cryst.* **E68**, o3172.
- Rivera, A. & Quevedo, R. (2004). *Tetrahedron Lett.* **45**, 8335–8338.
- Rivera, A. & Quevedo, R. (2013). *Tetrahedron Lett.* **54**, 1416–1420.
- Rivera, A., Quevedo, R., Navarro, M. A. & Maldonado, M. (2004). *Synth. Commun.* **34**, 2479–2485.
- Rivera, A., Quiroga, D., Ríos-Motta, J., Kučeráková, M. & Dušek, M. (2013). *Acta Cryst.* **E69**, o217.
- Rivera, A., Ríos-Motta, J., Quevedo, R. & Joseph-Nathan, P. (2005). *Rev. Col. Quím.* **34**, 105–115.
- Rivera, A., Sadat-Bernal, J., Ríos-Motta, J., Pojarová, M. & Dušek, M. (2011). *Acta Cryst.* **E67**, o2581.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Stoe & Cie (2001). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.

supporting information

Acta Cryst. (2015). E71, 312-314 [doi:10.1107/S2056989015002212]

Crystal structure of the di-Mannich base 4,4'-dichloro-3,3',5,5'-tetramethyl-2,2'-[imidazolidine-1,3-diylbis(methylene)]diphenol

Augusto Rivera, Luz Stella Nerio and Michael Bolte

Computing details

Data collection: *X-AREA* and *X-RED32* (Stoe & Cie, 2001); cell refinement: *X-AREA* and *X-RED32* (Stoe & Cie, 2001); data reduction: *X-AREA* and *X-RED32* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS87* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

4,4'-Dichloro-3,3',5,5'-tetramethyl-2,2'-[imidazolidine-1,3-diylbis(methylene)]diphenol

Crystal data

$C_{21}H_{26}Cl_2N_2O_2$

$M_r = 409.34$

Orthorhombic, *Pna*2₁

$a = 20.1594$ (11) Å

$b = 17.8088$ (12) Å

$c = 5.6120$ (3) Å

$V = 2014.8$ (2) Å³

$Z = 4$

$F(000) = 864$

$D_x = 1.349$ Mg m⁻³

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

Cell parameters from 16491 reflections

$\theta = 2.1$ – 25.9°

$\mu = 0.34$ mm⁻¹

$T = 173$ K

Needle, colourless

$0.22 \times 0.11 \times 0.09$ mm

Data collection

Stoe IPDS II two-circle diffractometer

Radiation source: Genix 3D I μ S microfocus X-ray source

ω scans

Absorption correction: multi-scan (*X-AREA*; Stoe & Cie, 2001)

$T_{\min} = 0.891$, $T_{\max} = 0.946$

17730 measured reflections

3708 independent reflections

3280 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.080$

$\theta_{\max} = 25.4^\circ$, $\theta_{\min} = 2.0^\circ$

$h = -24 \rightarrow 24$

$k = -21 \rightarrow 21$

$l = -6 \rightarrow 6$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.082$

$S = 1.00$

3708 reflections

256 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2]$

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

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

$\Delta\rho_{\max} = 0.16$ e Å⁻³

$\Delta\rho_{\min} = -0.20$ e Å⁻³

Absolute structure: Flack x determined using

1338 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.00 (4)

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.71322 (3)	0.87262 (4)	0.49746 (17)	0.04042 (19)
C12	0.63887 (4)	0.04441 (4)	0.5199 (2)	0.0535 (2)
O1	0.55382 (11)	0.60445 (11)	0.6973 (4)	0.0383 (5)
H1	0.574 (2)	0.565 (3)	0.595 (9)	0.074 (13)*
O2	0.52557 (10)	0.34212 (11)	0.6988 (4)	0.0368 (5)
H2	0.5460 (19)	0.3744 (19)	0.611 (7)	0.044 (10)*
N1	0.62589 (11)	0.52659 (13)	0.4013 (5)	0.0304 (5)
N2	0.61125 (12)	0.40126 (13)	0.4025 (5)	0.0308 (5)
C1	0.60746 (16)	0.46539 (14)	0.2433 (5)	0.0326 (6)
H1A	0.5620	0.4721	0.1797	0.039*
H1B	0.6390	0.4605	0.1090	0.039*
C2	0.68434 (15)	0.49812 (15)	0.5313 (7)	0.0394 (7)
H2A	0.6872	0.5204	0.6925	0.047*
H2B	0.7258	0.5092	0.4435	0.047*
C3	0.67177 (14)	0.41297 (15)	0.5448 (6)	0.0341 (7)
H3A	0.7096	0.3846	0.4768	0.041*
H3B	0.6649	0.3968	0.7118	0.041*
C4	0.63685 (15)	0.59859 (15)	0.2782 (6)	0.0337 (6)
H4A	0.6020	0.6056	0.1558	0.040*
H4B	0.6803	0.5971	0.1959	0.040*
C5	0.60838 (15)	0.32829 (16)	0.2813 (6)	0.0337 (6)
H5A	0.6508	0.3195	0.1969	0.040*
H5B	0.5725	0.3294	0.1608	0.040*
C11	0.63568 (13)	0.66441 (15)	0.4475 (5)	0.0290 (6)
C12	0.59219 (13)	0.66519 (15)	0.6419 (6)	0.0304 (6)
C13	0.58553 (14)	0.72820 (15)	0.7842 (6)	0.0332 (6)
H13	0.5558	0.7269	0.9154	0.040*
C14	0.62147 (14)	0.79335 (15)	0.7393 (6)	0.0326 (7)
C15	0.66605 (13)	0.79115 (14)	0.5501 (6)	0.0308 (6)
C16	0.67502 (13)	0.72850 (15)	0.4053 (5)	0.0296 (6)
C17	0.61244 (17)	0.86156 (17)	0.8953 (7)	0.0429 (8)
H17A	0.5790	0.8509	1.0175	0.064*
H17B	0.5977	0.9040	0.7976	0.064*
H17C	0.6547	0.8741	0.9720	0.064*
C18	0.72556 (15)	0.72805 (16)	0.2061 (6)	0.0387 (7)
H18A	0.7530	0.7733	0.2163	0.058*
H18B	0.7026	0.7270	0.0522	0.058*
H18C	0.7538	0.6835	0.2208	0.058*
C21	0.59596 (13)	0.26437 (14)	0.4523 (5)	0.0299 (6)

C22	0.55305 (14)	0.27410 (15)	0.6465 (6)	0.0317 (6)
C23	0.53458 (15)	0.21404 (16)	0.7892 (6)	0.0351 (6)
H23	0.5045	0.2221	0.9169	0.042*
C24	0.55924 (16)	0.14239 (16)	0.7492 (6)	0.0385 (7)
C25	0.60474 (15)	0.13394 (15)	0.5636 (6)	0.0359 (7)
C26	0.62373 (14)	0.19245 (16)	0.4129 (6)	0.0334 (7)
C27	0.67213 (16)	0.18022 (16)	0.2127 (6)	0.0405 (7)
H27A	0.6872	0.1279	0.2141	0.061*
H27B	0.7103	0.2137	0.2333	0.061*
H27C	0.6504	0.1911	0.0604	0.061*
C28	0.5373 (2)	0.07780 (19)	0.9026 (7)	0.0534 (9)
H28A	0.5161	0.0395	0.8029	0.080*
H28B	0.5056	0.0958	1.0220	0.080*
H28C	0.5759	0.0560	0.9829	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0421 (4)	0.0336 (3)	0.0456 (4)	−0.0080 (3)	0.0053 (4)	−0.0003 (4)
C12	0.0674 (5)	0.0306 (3)	0.0625 (6)	0.0073 (3)	−0.0007 (6)	0.0026 (4)
O1	0.0401 (11)	0.0349 (10)	0.0400 (14)	−0.0082 (9)	0.0115 (10)	0.0021 (9)
O2	0.0379 (11)	0.0373 (11)	0.0353 (13)	0.0040 (9)	0.0028 (10)	0.0014 (10)
N1	0.0329 (12)	0.0293 (11)	0.0289 (13)	−0.0008 (9)	−0.0042 (11)	0.0015 (10)
N2	0.0352 (13)	0.0284 (11)	0.0287 (13)	0.0008 (9)	−0.0056 (11)	0.0000 (10)
C1	0.0389 (15)	0.0314 (14)	0.0276 (17)	−0.0011 (11)	−0.0055 (13)	0.0012 (12)
C2	0.0415 (15)	0.0360 (14)	0.041 (2)	−0.0018 (12)	−0.0137 (17)	0.0032 (15)
C3	0.0362 (15)	0.0345 (13)	0.0316 (18)	0.0020 (11)	−0.0093 (13)	−0.0026 (13)
C4	0.0397 (16)	0.0294 (14)	0.0319 (17)	−0.0007 (11)	0.0015 (14)	0.0043 (12)
C5	0.0385 (15)	0.0328 (14)	0.0297 (17)	−0.0006 (12)	−0.0014 (13)	−0.0034 (13)
C11	0.0294 (14)	0.0299 (13)	0.0278 (18)	0.0023 (10)	−0.0001 (12)	0.0028 (11)
C12	0.0277 (14)	0.0317 (13)	0.0316 (17)	0.0003 (11)	0.0017 (12)	0.0036 (12)
C13	0.0314 (14)	0.0368 (14)	0.0314 (17)	0.0021 (12)	0.0052 (13)	0.0011 (12)
C14	0.0320 (14)	0.0318 (14)	0.0342 (19)	0.0028 (10)	−0.0001 (13)	−0.0008 (13)
C15	0.0286 (13)	0.0298 (13)	0.0341 (18)	−0.0021 (10)	−0.0026 (12)	0.0020 (12)
C16	0.0268 (13)	0.0325 (14)	0.0294 (16)	0.0033 (11)	0.0004 (12)	0.0048 (11)
C17	0.0484 (18)	0.0375 (16)	0.043 (2)	0.0007 (13)	0.0080 (16)	−0.0055 (14)
C18	0.0394 (16)	0.0375 (15)	0.0392 (19)	−0.0023 (12)	0.0099 (15)	−0.0007 (13)
C21	0.0295 (13)	0.0308 (13)	0.0294 (18)	−0.0022 (11)	−0.0035 (12)	−0.0018 (11)
C22	0.0309 (14)	0.0345 (14)	0.0297 (17)	0.0005 (11)	−0.0053 (12)	−0.0020 (12)
C23	0.0337 (15)	0.0418 (16)	0.0297 (16)	−0.0032 (12)	0.0003 (13)	0.0006 (13)
C24	0.0450 (17)	0.0352 (15)	0.0352 (19)	−0.0093 (12)	−0.0069 (15)	0.0043 (13)
C25	0.0403 (15)	0.0295 (13)	0.038 (2)	−0.0003 (11)	−0.0085 (13)	−0.0005 (12)
C26	0.0309 (14)	0.0346 (15)	0.0347 (17)	−0.0020 (11)	−0.0047 (13)	−0.0045 (12)
C27	0.0421 (17)	0.0390 (16)	0.040 (2)	0.0014 (13)	0.0049 (15)	−0.0065 (14)
C28	0.065 (2)	0.0424 (18)	0.053 (2)	−0.0127 (16)	0.0006 (19)	0.0101 (16)

Geometric parameters (Å, °)

C11—C15	1.760 (3)	C13—C14	1.391 (4)
C12—C25	1.754 (3)	C13—H13	0.9500
O1—C12	1.366 (3)	C14—C15	1.392 (4)
O1—H1	0.99 (5)	C14—C17	1.508 (4)
O2—C22	1.364 (3)	C15—C16	1.392 (4)
O2—H2	0.86 (4)	C16—C18	1.513 (4)
N1—C1	1.453 (4)	C17—H17A	0.9800
N1—C4	1.473 (4)	C17—H17B	0.9800
N1—C2	1.476 (4)	C17—H17C	0.9800
N2—C1	1.452 (3)	C18—H18A	0.9800
N2—C5	1.468 (4)	C18—H18B	0.9800
N2—C3	1.473 (4)	C18—H18C	0.9800
C1—H1A	0.9900	C21—C22	1.402 (4)
C1—H1B	0.9900	C21—C26	1.415 (4)
C2—C3	1.539 (4)	C22—C23	1.387 (4)
C2—H2A	0.9900	C23—C24	1.388 (4)
C2—H2B	0.9900	C23—H23	0.9500
C3—H3A	0.9900	C24—C25	1.396 (5)
C3—H3B	0.9900	C24—C28	1.503 (4)
C4—C11	1.509 (4)	C25—C26	1.396 (4)
C4—H4A	0.9900	C26—C27	1.504 (5)
C4—H4B	0.9900	C27—H27A	0.9800
C5—C21	1.510 (4)	C27—H27B	0.9800
C5—H5A	0.9900	C27—H27C	0.9800
C5—H5B	0.9900	C28—H28A	0.9800
C11—C12	1.399 (4)	C28—H28B	0.9800
C11—C16	1.410 (4)	C28—H28C	0.9800
C12—C13	1.384 (4)		
C12—O1—H1	101 (3)	C15—C14—C17	122.9 (3)
C22—O2—H2	106 (2)	C14—C15—C16	123.5 (2)
C1—N1—C4	113.9 (2)	C14—C15—C11	117.0 (2)
C1—N1—C2	104.4 (2)	C16—C15—C11	119.5 (2)
C4—N1—C2	114.3 (2)	C15—C16—C11	118.5 (3)
C1—N2—C5	114.2 (2)	C15—C16—C18	121.5 (3)
C1—N2—C3	105.4 (2)	C11—C16—C18	119.9 (3)
C5—N2—C3	114.2 (2)	C14—C17—H17A	109.5
N2—C1—N1	101.6 (2)	C14—C17—H17B	109.5
N2—C1—H1A	111.5	H17A—C17—H17B	109.5
N1—C1—H1A	111.5	C14—C17—H17C	109.5
N2—C1—H1B	111.5	H17A—C17—H17C	109.5
N1—C1—H1B	111.5	H17B—C17—H17C	109.5
H1A—C1—H1B	109.3	C16—C18—H18A	109.5
N1—C2—C3	103.4 (2)	C16—C18—H18B	109.5
N1—C2—H2A	111.1	H18A—C18—H18B	109.5
C3—C2—H2A	111.1	C16—C18—H18C	109.5

N1—C2—H2B	111.1	H18A—C18—H18C	109.5
C3—C2—H2B	111.1	H18B—C18—H18C	109.5
H2A—C2—H2B	109.1	C22—C21—C26	118.5 (3)
N2—C3—C2	104.4 (2)	C22—C21—C5	120.2 (2)
N2—C3—H3A	110.9	C26—C21—C5	121.2 (3)
C2—C3—H3A	110.9	O2—C22—C23	116.8 (3)
N2—C3—H3B	110.9	O2—C22—C21	121.9 (3)
C2—C3—H3B	110.9	C23—C22—C21	121.3 (3)
H3A—C3—H3B	108.9	C22—C23—C24	121.3 (3)
N1—C4—C11	112.2 (3)	C22—C23—H23	119.4
N1—C4—H4A	109.2	C24—C23—H23	119.4
C11—C4—H4A	109.2	C23—C24—C25	117.1 (3)
N1—C4—H4B	109.2	C23—C24—C28	120.4 (3)
C11—C4—H4B	109.2	C25—C24—C28	122.6 (3)
H4A—C4—H4B	107.9	C26—C25—C24	123.5 (3)
N2—C5—C21	112.3 (2)	C26—C25—C12	119.1 (2)
N2—C5—H5A	109.1	C24—C25—C12	117.4 (2)
C21—C5—H5A	109.1	C25—C26—C21	118.2 (3)
N2—C5—H5B	109.1	C25—C26—C27	121.5 (3)
C21—C5—H5B	109.1	C21—C26—C27	120.3 (3)
H5A—C5—H5B	107.9	C26—C27—H27A	109.5
C12—C11—C16	118.4 (3)	C26—C27—H27B	109.5
C12—C11—C4	120.6 (2)	H27A—C27—H27B	109.5
C16—C11—C4	120.9 (3)	C26—C27—H27C	109.5
O1—C12—C13	117.1 (3)	H27A—C27—H27C	109.5
O1—C12—C11	121.6 (3)	H27B—C27—H27C	109.5
C13—C12—C11	121.2 (3)	C24—C28—H28A	109.5
C12—C13—C14	121.4 (3)	C24—C28—H28B	109.5
C12—C13—H13	119.3	H28A—C28—H28B	109.5
C14—C13—H13	119.3	C24—C28—H28C	109.5
C13—C14—C15	116.8 (3)	H28A—C28—H28C	109.5
C13—C14—C17	120.3 (3)	H28B—C28—H28C	109.5
C5—N2—C1—N1	-168.1 (2)	C14—C15—C16—C18	-178.2 (3)
C3—N2—C1—N1	-42.0 (3)	C11—C15—C16—C18	1.3 (4)
C4—N1—C1—N2	170.7 (2)	C12—C11—C16—C15	-3.7 (4)
C2—N1—C1—N2	45.4 (3)	C4—C11—C16—C15	172.2 (3)
C1—N1—C2—C3	-31.0 (3)	C12—C11—C16—C18	176.3 (3)
C4—N1—C2—C3	-156.0 (2)	C4—C11—C16—C18	-7.8 (4)
C1—N2—C3—C2	22.5 (3)	N2—C5—C21—C22	37.3 (4)
C5—N2—C3—C2	148.6 (3)	N2—C5—C21—C26	-146.7 (3)
N1—C2—C3—N2	5.2 (3)	C26—C21—C22—O2	178.5 (3)
C1—N1—C4—C11	163.0 (2)	C5—C21—C22—O2	-5.4 (4)
C2—N1—C4—C11	-77.2 (3)	C26—C21—C22—C23	-4.0 (4)
C1—N2—C5—C21	-166.3 (2)	C5—C21—C22—C23	172.1 (3)
C3—N2—C5—C21	72.3 (3)	O2—C22—C23—C24	179.3 (3)
N1—C4—C11—C12	-36.2 (4)	C21—C22—C23—C24	1.7 (5)
N1—C4—C11—C16	148.0 (2)	C22—C23—C24—C25	1.7 (4)

C16—C11—C12—O1	-178.3 (3)	C22—C23—C24—C28	-178.6 (3)
C4—C11—C12—O1	5.8 (4)	C23—C24—C25—C26	-3.0 (5)
C16—C11—C12—C13	2.7 (4)	C28—C24—C25—C26	177.3 (3)
C4—C11—C12—C13	-173.2 (3)	C23—C24—C25—C12	177.3 (2)
O1—C12—C13—C14	-178.7 (3)	C28—C24—C25—C12	-2.4 (4)
C11—C12—C13—C14	0.3 (5)	C24—C25—C26—C21	0.8 (5)
C12—C13—C14—C15	-2.2 (4)	C12—C25—C26—C21	-179.5 (2)
C12—C13—C14—C17	179.1 (3)	C24—C25—C26—C27	-179.0 (3)
C13—C14—C15—C16	1.2 (4)	C12—C25—C26—C27	0.7 (4)
C17—C14—C15—C16	179.8 (3)	C22—C21—C26—C25	2.7 (4)
C13—C14—C15—C11	-178.4 (2)	C5—C21—C26—C25	-173.4 (3)
C17—C14—C15—C11	0.3 (4)	C22—C21—C26—C27	-177.5 (3)
C14—C15—C16—C11	1.8 (4)	C5—C21—C26—C27	6.4 (4)
C11—C15—C16—C11	-178.7 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...N1	0.99 (5)	1.66 (5)	2.606 (3)	158 (4)
O2—H2...N2	0.86 (4)	1.83 (4)	2.619 (3)	152 (3)
C13—H13...O2 ⁱ	0.95	2.59	3.464 (4)	152

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