Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of the co-crystalline adduct 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD)–4-chloro-3,5-dimethylphenol (1/1)

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Received 12 May 2015
Accepted 27 May 2015

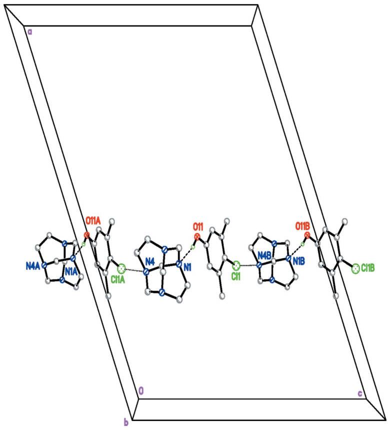
Edited by G. Smith, Queensland University of Technology, Australia

Keywords: crystal structure; co-crystalline adducts; TATD; hydrogen bonding; C—H$\cdots\pi$ interactions

CCDC reference: 1403518

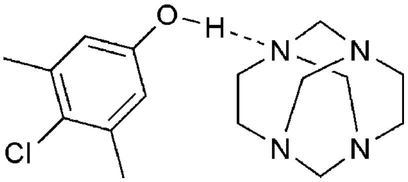
Supporting information: this article has supporting information at journals.iucr.org/e

In the crystal of the title co-crystalline adduct, $C_8H_{16}N_4{\cdot}C_8H_9ClO$, (I), prepared by solid-state reaction, the molecules are linked by intermolecular O—H$\cdots$N hydrogen bonds, forming a *D* motif. The azaadamantane structure in (I) is slightly distorted, with N—CH$_2$—CH$_2$—N torsion angles of 10.4 (3) and −9.0 (3)°. These values differ slightly from the corresponding torsion angles in the free aminal cage (0.0°) and in related co-crystalline adducts, which are not far from a planar geometry and consistent with a D_{2d} molecular symmetry in the tetraazatricyclo structure. The structures also differ in that there is a slight elongation of the N—C bond lengths about the N atom that accepts the hydrogen bond in (I) compared with the other N—C bond lengths. In the crystal, the two molecules are not only linked by a classical O—H$\cdots$N hydrogen bond but are further connected by weak C—H$\cdots\pi$ interactions, forming a two-dimensional supramolecular network parallel to the *bc* plane.



1. Chemical context

In our continuing investigations on the reactivity of cyclic aminals of the adamantane type with phenols, we have found that 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD) shows an interesting reactivity with 4-chloro-3,5-dimethylphenol under different conditions. Reaction between TATD with 4-chloro-3,5-dimethylphenol in solution yields symmetrical bis-benzoxazines (Rivera *et al.*, 2005), but under heating in an oil bath (Rivera & Quevedo, 2013) or microwave-assisted solvent-free conditions, symmetrical *N*,*N*'-disubstituted imidazolidines (Rivera, Nerio & Bolte, 2015) are obtained. Therefore, we became interested in exploring the reactivity of TATD with phenols under solvent-free conditions at room temperature. In the course of our investigations, we obtained the molecular salt 8,10,12-triaza-1-azoniatetracyclo-[8.3.1.1^{8,12}.0^{2,7}]pentadecane 4-nitrophenolate 4-nitrophenol by grinding (2*R*,7*R*)-1,8,10,12-tetraazatetracyclo[8.3.1.1^{8,12}.0^{2,7}]-pentadecane with 4-nitrophenol (Rivera, Uribe, Ríos-Motta *et al.*, 2015) and the 1:2 adduct 1,3,6,8-tetraazatricyclo-[4.4.1.1^{3,8}]dodecane (TATD)-4-bromophenol (Rivera, Uribe, Rojas *et al.*, 2015) by grinding at room temperature.



Herein, we describe the synthesis of the title co-crystalline adduct 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD)–

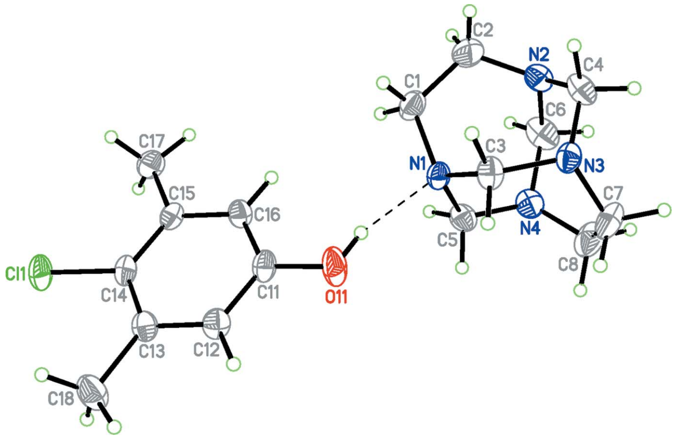


Figure 1
Perspective view of the title compound, with displacement ellipsoids drawn at the 50% probability level. The hydrogen bond is drawn as a dashed line.

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.470 (2)	N3—C7	1.455 (2)
N1—C5	1.470 (2)	N3—C4	1.458 (2)
N1—C3	1.480 (2)	N4—C5	1.444 (2)
N2—C2	1.449 (3)	N4—C6	1.456 (2)
N2—C6	1.454 (3)	N4—C8	1.457 (3)
N2—C4	1.462 (2)	Cl1—C14	1.7534 (16)
N3—C3	1.446 (2)	O11—C11	1.356 (2)
N1—C1—C2—N2	10.4 (3)	N3—C7—C8—N4	−9.0 (3)

Table 2
Hydrogen-bond geometry (Å, °).

*Cg*8 is the centroid of the C11–C16 ring.

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O11—H11⋯N1	0.85 (4)	1.92 (4)	2.752 (2)	165 (3)
C3—H3*A*⋯*Cg*8^{i}	0.99	2.89	3.837 (2)	160
C8—H8*A*⋯*Cg*8^{ii}	0.99	2.88	3.814 (2)	157

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

4-chloro-3,5-dimethylphenol under solvent-free conditions by simply grinding together the components at room temperature.

2. Structural commentary

The crystal structure of the title compound, (I), has confirmed the presence of a 1:1 co-crystalline adduct. A view of this adduct is shown in Fig. 1. The asymmetric unit of the title compound contains a 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]-dodecane (TATD) and a 4-chloro-3,5-dimethylphenol molecule linked *via* an O—H⋯N hydrogen bond, forming a *D* motif (Bernstein *et al.*, 1995). As in the 1:2 adduct with 4-bromophenol (Rivera, Uribe, Rojas *et al.*, 2015) and the 1:1 adduct with hydroquinone (Rivera *et al.*, 2007), the intermolecular O—H⋯N hydrogen bond in (I) also leads to a stable supramolecular structure, but comparison of the title compound with the above-mentioned related structures shows that the three adducts differ in the O⋯N hydrogen-bond distances [2.752 (2) Å in (I), 2.705 (5) Å in the 1:2 adduct and 2.767 (2) Å in the co-crystalline adduct with hydroquinone], which is in agreement with the differences in the p*K*a values between the species involved in the hydrogen bond (Majerz *et al.*, 1997): 4-chloro-3,5-dimethylphenol (p*K*a = 9.76); *p*-bromophenol (p*K*a = 9.37) and hydroquinone (p*K*a = 9.85) (Lide, 2003).

To a first approximation, the geometric parameters of the title molecule agree well with those reported for similar structures (Rivera *et al.*, 2007; Rivera, Uribe, Rojas *et al.*, 2015) and are within normal ranges (Allen *et al.*, 1987), but compared to the free aminal cage structure (Rivera *et al.*, 2014) which belongs to the D_{2d} point group, two small differences are noted. The azaadamantane structure in (I) is slightly distorted, with N—CH$_2$_CH$_2$—N torsion angles of 10.4 (3)° (N1—C1—C2—N2) and −9.0 (3)° (N3—C7—C8—N4). These values differ slightly from the values of the corresponding torsion angles in the free aminal cage (0.0°; Rivera *et al.*, 2014), and the related co-crystalline adducts [2.4 (7)° (Rivera, Uribe, Rojas *et al.*, 2015) and −0.62° (Rivera *et al.*, 2007)] which shows that each N—C—C—N group is not far from a planar geometry and consistent with a D_{2d} molecular symmetry in the tetraazatricyclo structure. Furthermore, the structures also differ in the slight elongation of the N1—C bond lengths of the nitrogen atom that accepts the hydrogen bond, [1.470 (2) and 1.480 (2) Å], compared to the the other N—C bond lengths (Table 1).

3. Supramolecular features

The two different molecules in (I) are connected by a classical O—H⋯N hydrogen bond. The crystal packing is further stabilized by weak intermolecular C—H⋯π interactions, linking the molecules into two-dimensional sheets in the *bc* plane (Table 2 and Fig. 2). Furthermore, there are short N⋯Cl contacts [N4⋯Cl1^{i} 3.1680 (15) Å; symmetry operator: (i) $x, -y, z-\frac{1}{2}$] linking the molecules into zigzag chains running along the *c*-axis direction (Fig. 3).

4. Database survey

The geometric parameters of 4-chloro-3,5-dimethylphenol in (I) (Table 1) agree well with those of found in the crystal structure containing only this molecule (Cox, 1995), which crystallized with two molecules in the asymmetric unit [C—O = 1.387 (3) and 1.378 (3) Å; C—Cl = 1.752 (2) and 1.749 (2) Å; C—C$_{\rm methyl}$ = 1.502 (3), 1.500 (3), 1.514 (3) and 1.505 (3) Å]. For 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane, two comparable structures were retrieved from the CSD (Groom & Allen, 2014). A least-squares fit of the structure that contains only 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (Rivera *et al.*, 2014) gives an r.m.s. deviation of 0.048 Å with 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane of (I) and a least-squares fit of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane co-crystallized with

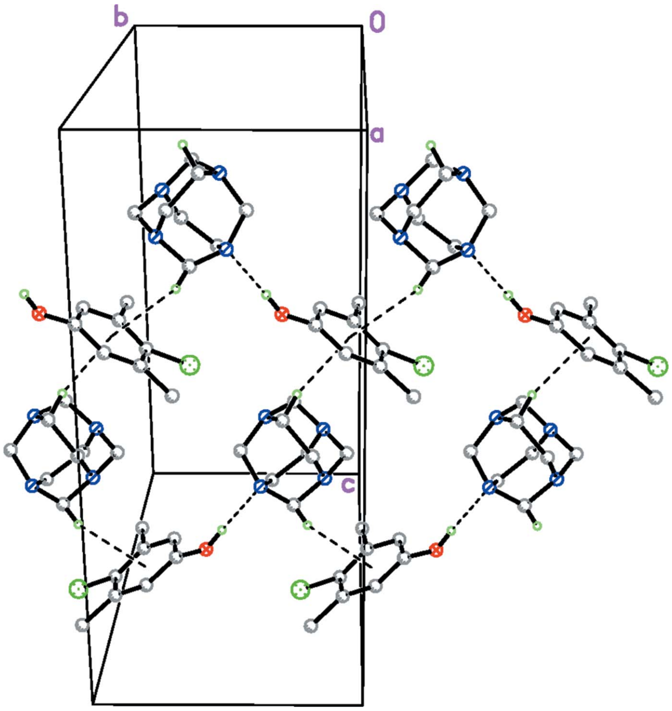


Figure 2
Packing diagram of the title compound. Only H atoms involved in hydrogen bonding are shown. Hydrogen bonds are drawn as dashed lines.

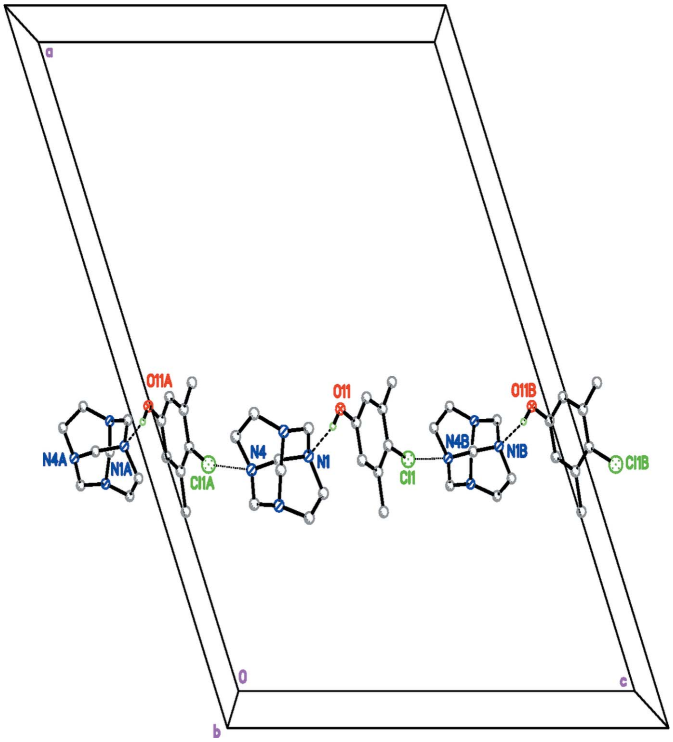


Figure 3
Partial packing diagram of the title compound, viewed along the *b* axis. Only H atoms involved in hydrogen bonding are shown. Hydrogen bonds are drawn as dashed lines and the short Cl$\cdots$N contacts are shown as dotted lines. Atoms with suffix A are generated by the symmetry operator (x, $-y$, $z - \frac{1}{2}$) and atoms with suffix B are generated by the symmetry operator (x, $-y$, $z + \frac{1}{2}$).

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_8H_{16}N_4 \cdot C_8H_9ClO$
M_r	324.85
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	173
a, *b*, *c* (Å)	25.6048 (18), 7.5295 (7), 18.2317 (13)
β (°)	111.080 (5)
V (Å^3)	3279.7 (5)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.24
Crystal size (mm)	0.27 × 0.26 × 0.22
Data collection	
Diffractometer	Stoe *IPDS* II two-circle
Absorption correction	Multi-scan (*X-RED32*; Stoe & Cie, 2001)
$T_{\min}$, $T_{\max}$	0.738, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14414, 3066, 2512
$R_{\rm int}$	0.083
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.608
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.107, 1.02
No. of reflections	3066
No. of parameters	205
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.26, −0.25

Computer programs: *X-AREA* (Stoe & Cie, 2001), *SHELXS97* and *XP* in *SHELXTL-Plus* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

hydroquinone (Rivera *et al.*, 2007) gives an r.m.s. deviation of 0.051 Å with 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane of (I). Thus, it can be concluded that the conformational freedom of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane is rather limited.

5. Synthesis and crystallization

A mixture of 1,3,6,8-tetraazatricyclo[4.4.1.^{3,8}]dodecane (TATD) (168 mg, 1 mmol) and 4-chloro-3,5-dimethylphenol (157 mg, 1 mmol) was ground using a mortar and pestle, at room temperature for 15 min., as required to complete the reaction (TLC). The mixture was then dissolved in methanol. Crystals suitable for X-ray diffraction were obtained from a methanol solution upon slow evaporation of the solvent at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were located in difference electron-density maps. The hydroxyl H atom was refined freely, while C-bound H atoms were fixed geometrically (C—H = 0.95, 0.98 or 0.99 Å) and refined using a riding model, with $U_{\rm iso}$(H) values set at 1.2$U_{\rm eq}$ (1.5 for methyl groups) of the parent atom. The methyl groups were allowed to rotate but not to tip.

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Acknowledgements

We acknowledge the financial support provided to us by the Dirección de Investigación, Sede Bogotá (DIB) at the Universidad Nacional de Colombia. JJR thanks COLCIENCIAS for a fellowship.

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supporting information

Acta Cryst. (2015). E**71**, 737-740 [doi:10.1107/S2056989015010257]

Crystal structure of the co-crystalline adduct 1,3,6,8-tetraazatricyclo-[4.4.1.1^{3,8}]dodecane (TATD)–4-chloro-3,5-dimethylphenol (1/1)

Augusto Rivera, Jicli José Rojas, Jaime Ríos-Motta and Michael Bolte

Computing details

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA* (Stoe & Cie, 2001); data reduction: *X-AREA* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (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).

1,3,6,8-Tetraazatricyclo[4.4.1.1^{3,8}]dodecane; 4-chloro-3,5-dimethylphenol

Crystal data

$C_8H_{16}N_4 \cdot C_8H_9ClO$	$F(000) = 1392$
$M_r = 324.85$	$D_x = 1.316$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 25.6048$ (18) Å	Cell parameters from 12525 reflections
$b = 7.5295$ (7) Å	$\theta = 3.4$–25.8°
$c = 18.2317$ (13) Å	$\mu = 0.24$ mm^{-1}
$\beta = 111.080$ (5)°	$T = 173$ K
$V = 3279.7$ (5) Å^3	Block, colourless
$Z = 8$	$0.27 \times 0.26 \times 0.22$ mm

Data collection

Stoe IPDS II two-circle diffractometer	14414 measured reflections
Radiation source: Genix 3D IμS microfocus X-ray source	3066 independent reflections
ω scans	2512 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*X-RED32*; Stoe & Cie, 2001)	$R_{\text{int}} = 0.083$
$T_{\text{min}} = 0.738$, $T_{\text{max}} = 1.000$	$\theta_{\text{max}} = 25.6$°, $\theta_{\text{min}} = 3.4$°
	$h = -30 \rightarrow 30$
	$k = -9 \rightarrow 9$
	$l = -19 \rightarrow 22$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.5777P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.107$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.26$ e Å^{-3}
3066 reflections	$\Delta\rho_{\text{min}} = -0.25$ e Å^{-3}
205 parameters	
0 restraints	

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 (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
N1	0.37029 (5)	0.56339 (18)	0.36779 (8)	0.0224 (3)
N2	0.30414 (6)	0.8359 (2)	0.26828 (9)	0.0297 (3)
N3	0.40890 (6)	0.84503 (19)	0.33226 (9)	0.0260 (3)
N4	0.35050 (6)	0.58696 (19)	0.22295 (9)	0.0299 (3)
C1	0.31697 (7)	0.6087 (2)	0.37648 (11)	0.0313 (4)
H1A	0.3246	0.6345	0.4326	0.038*
H1B	0.2924	0.5030	0.3623	0.038*
C2	0.28501 (8)	0.7651 (3)	0.32812 (14)	0.0438 (5)
H2A	0.2455	0.7287	0.3022	0.053*
H2B	0.2857	0.8627	0.3649	0.053*
C3	0.41163 (7)	0.7098 (2)	0.38985 (10)	0.0267 (4)
H3A	0.4084	0.7700	0.4363	0.032*
H3B	0.4494	0.6559	0.4068	0.032*
C4	0.35575 (8)	0.9394 (2)	0.29998 (12)	0.0333 (4)
H4A	0.3578	1.0180	0.2575	0.040*
H4B	0.3524	1.0170	0.3419	0.040*
C5	0.36300 (7)	0.4777 (2)	0.29227 (11)	0.0285 (4)
H5A	0.3977	0.4111	0.2989	0.034*
H5B	0.3325	0.3894	0.2818	0.034*
C6	0.30356 (8)	0.7083 (3)	0.20810 (12)	0.0376 (5)
H6A	0.2997	0.7761	0.1599	0.045*
H6B	0.2693	0.6355	0.1961	0.045*
C7	0.43347 (9)	0.7933 (3)	0.27484 (12)	0.0386 (5)
H7A	0.4705	0.7391	0.3032	0.046*
H7B	0.4399	0.9020	0.2487	0.046*
C8	0.39926 (10)	0.6640 (3)	0.21162 (13)	0.0430 (5)
H8A	0.3865	0.7265	0.1604	0.052*
H8B	0.4241	0.5661	0.2084	0.052*
Cl1	0.35337 (2)	−0.26689 (6)	0.61168 (3)	0.03412 (16)
O11	0.43692 (5)	0.32897 (19)	0.47753 (9)	0.0390 (4)
H11	0.4116 (15)	0.396 (5)	0.447 (2)	0.084 (10)*
C11	0.41519 (7)	0.1923 (2)	0.50578 (10)	0.0257 (4)
C12	0.45255 (7)	0.0659 (2)	0.55103 (10)	0.0261 (4)
H12	0.4913	0.0774	0.5597	0.031*
C13	0.43430 (7)	−0.0768 (2)	0.58371 (10)	0.0250 (4)
C14	0.37708 (7)	−0.0899 (2)	0.56943 (10)	0.0237 (3)
C15	0.33830 (7)	0.0318 (2)	0.52312 (10)	0.0229 (3)
C16	0.35825 (7)	0.1742 (2)	0.49162 (10)	0.0245 (4)
H16	0.3327	0.2597	0.4601	0.029*

C17	0.27635 (7)	0.0110 (2)	0.50600 (12)	0.0311 (4)
H17A	0.2638	−0.1047	0.4813	0.047*
H17B	0.2559	0.1057	0.4704	0.047*
H17C	0.2692	0.0185	0.5552	0.047*
C18	0.47576 (8)	−0.2148 (3)	0.63056 (13)	0.0388 (5)
H18A	0.4719	−0.2311	0.6817	0.058*
H18B	0.5139	−0.1753	0.6384	0.058*
H18C	0.4684	−0.3277	0.6019	0.058*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0202 (6)	0.0238 (7)	0.0228 (7)	−0.0040 (5)	0.0074 (5)	0.0018 (5)
N2	0.0289 (7)	0.0269 (7)	0.0311 (8)	0.0034 (6)	0.0080 (6)	0.0026 (6)
N3	0.0285 (7)	0.0250 (7)	0.0264 (8)	−0.0061 (6)	0.0122 (6)	−0.0009 (6)
N4	0.0394 (8)	0.0270 (7)	0.0227 (8)	−0.0012 (6)	0.0104 (6)	−0.0047 (6)
C1	0.0261 (8)	0.0386 (10)	0.0328 (10)	−0.0012 (7)	0.0152 (8)	0.0041 (8)
C2	0.0350 (10)	0.0483 (11)	0.0558 (14)	0.0129 (9)	0.0259 (10)	0.0134 (10)
C3	0.0243 (8)	0.0289 (8)	0.0233 (9)	−0.0075 (6)	0.0042 (7)	0.0006 (7)
C4	0.0402 (10)	0.0206 (8)	0.0367 (11)	0.0003 (7)	0.0108 (8)	0.0009 (7)
C5	0.0331 (9)	0.0206 (8)	0.0309 (10)	−0.0020 (6)	0.0106 (7)	−0.0034 (7)
C6	0.0410 (10)	0.0353 (10)	0.0247 (10)	0.0032 (8)	−0.0024 (8)	−0.0014 (8)
C7	0.0408 (10)	0.0466 (11)	0.0376 (11)	−0.0112 (8)	0.0252 (9)	−0.0016 (9)
C8	0.0609 (13)	0.0429 (11)	0.0379 (12)	−0.0081 (10)	0.0333 (11)	−0.0079 (9)
Cl1	0.0372 (2)	0.0318 (2)	0.0342 (3)	−0.00899 (18)	0.01382 (19)	0.00941 (18)
O11	0.0250 (6)	0.0406 (8)	0.0481 (9)	−0.0075 (6)	0.0090 (6)	0.0216 (7)
C11	0.0256 (8)	0.0271 (8)	0.0240 (9)	−0.0081 (7)	0.0084 (7)	0.0023 (7)
C12	0.0194 (7)	0.0308 (9)	0.0256 (9)	−0.0054 (6)	0.0049 (6)	0.0012 (7)
C13	0.0267 (8)	0.0260 (8)	0.0197 (8)	−0.0027 (6)	0.0051 (7)	0.0003 (6)
C14	0.0298 (8)	0.0231 (8)	0.0189 (8)	−0.0077 (6)	0.0096 (7)	−0.0009 (6)
C15	0.0251 (8)	0.0253 (8)	0.0201 (8)	−0.0051 (6)	0.0102 (6)	−0.0028 (6)
C16	0.0240 (8)	0.0256 (8)	0.0220 (8)	−0.0011 (6)	0.0062 (7)	0.0033 (7)
C17	0.0255 (9)	0.0332 (9)	0.0373 (11)	−0.0038 (7)	0.0145 (7)	0.0008 (8)
C18	0.0325 (9)	0.0385 (10)	0.0387 (11)	0.0028 (8)	0.0047 (8)	0.0122 (9)

Geometric parameters (Å, º)

N1—C1	1.470 (2)	C7—C8	1.522 (3)
N1—C5	1.470 (2)	C7—H7A	0.9900
N1—C3	1.480 (2)	C7—H7B	0.9900
N2—C2	1.449 (3)	C8—H8A	0.9900
N2—C6	1.454 (3)	C8—H8B	0.9900
N2—C4	1.462 (2)	Cl1—C14	1.7534 (16)
N3—C3	1.446 (2)	O11—C11	1.356 (2)
N3—C7	1.455 (2)	O11—H11	0.85 (4)
N3—C4	1.458 (2)	C11—C12	1.391 (2)
N4—C5	1.444 (2)	C11—C16	1.393 (2)
N4—C6	1.456 (2)	C12—C13	1.388 (2)

N4—C8	1.457 (3)	C12—H12	0.9500
C1—C2	1.521 (3)	C13—C14	1.396 (2)
C1—H1A	0.9900	C13—C18	1.512 (2)
C1—H1B	0.9900	C14—C15	1.391 (2)
C2—H2A	0.9900	C15—C16	1.397 (2)
C2—H2B	0.9900	C15—C17	1.511 (2)
C3—H3A	0.9900	C16—H16	0.9500
C3—H3B	0.9900	C17—H17A	0.9800
C4—H4A	0.9900	C17—H17B	0.9800
C4—H4B	0.9900	C17—H17C	0.9800
C5—H5A	0.9900	C18—H18A	0.9800
C5—H5B	0.9900	C18—H18B	0.9800
C6—H6A	0.9900	C18—H18C	0.9800
C6—H6B	0.9900		

C1—N1—C5	113.12 (13)	N4—C6—H6B	107.5
C1—N1—C3	113.50 (13)	H6A—C6—H6B	107.0
C5—N1—C3	114.75 (13)	N3—C7—C8	115.84 (15)
C2—N2—C6	114.25 (16)	N3—C7—H7A	108.3
C2—N2—C4	113.62 (17)	C8—C7—H7A	108.3
C6—N2—C4	114.37 (16)	N3—C7—H7B	108.3
C3—N3—C7	114.43 (15)	C8—C7—H7B	108.3
C3—N3—C4	115.49 (14)	H7A—C7—H7B	107.4
C7—N3—C4	114.98 (16)	N4—C8—C7	115.87 (15)
C5—N4—C6	115.37 (15)	N4—C8—H8A	108.3
C5—N4—C8	114.79 (15)	C7—C8—H8A	108.3
C6—N4—C8	114.58 (16)	N4—C8—H8B	108.3
N1—C1—C2	116.37 (15)	C7—C8—H8B	108.3
N1—C1—H1A	108.2	H8A—C8—H8B	107.4
C2—C1—H1A	108.2	C11—O11—H11	112 (2)
N1—C1—H1B	108.2	O11—C11—C12	117.13 (15)
C2—C1—H1B	108.2	O11—C11—C16	123.30 (16)
H1A—C1—H1B	107.3	C12—C11—C16	119.58 (15)
N2—C2—C1	117.66 (15)	C13—C12—C11	121.22 (15)
N2—C2—H2A	107.9	C13—C12—H12	119.4
C1—C2—H2A	107.9	C11—C12—H12	119.4
N2—C2—H2B	107.9	C12—C13—C14	117.86 (15)
C1—C2—H2B	107.9	C12—C13—C18	119.89 (15)
H2A—C2—H2B	107.2	C14—C13—C18	122.22 (15)
N3—C3—N1	118.95 (14)	C15—C14—C13	122.59 (15)
N3—C3—H3A	107.6	C15—C14—Cl1	118.87 (12)
N1—C3—H3A	107.6	C13—C14—Cl1	118.54 (13)
N3—C3—H3B	107.6	C14—C15—C16	117.92 (14)
N1—C3—H3B	107.6	C14—C15—C17	121.63 (15)
H3A—C3—H3B	107.0	C16—C15—C17	120.45 (15)
N3—C4—N2	118.66 (14)	C11—C16—C15	120.81 (15)
N3—C4—H4A	107.6	C11—C16—H16	119.6
N2—C4—H4A	107.6	C15—C16—H16	119.6

N3—C4—H4B	107.6	C15—C17—H17A	109.5
N2—C4—H4B	107.6	C15—C17—H17B	109.5
H4A—C4—H4B	107.1	H17A—C17—H17B	109.5
N4—C5—N1	118.91 (13)	C15—C17—H17C	109.5
N4—C5—H5A	107.6	H17A—C17—H17C	109.5
N1—C5—H5A	107.6	H17B—C17—H17C	109.5
N4—C5—H5B	107.6	C13—C18—H18A	109.5
N1—C5—H5B	107.6	C13—C18—H18B	109.5
H5A—C5—H5B	107.0	H18A—C18—H18B	109.5
N2—C6—N4	119.39 (15)	C13—C18—H18C	109.5
N2—C6—H6A	107.5	H18A—C18—H18C	109.5
N4—C6—H6A	107.5	H18B—C18—H18C	109.5
N2—C6—H6B	107.5		

C5—N1—C1—C2	−73.2 (2)	C3—N3—C7—C8	74.7 (2)
C3—N1—C1—C2	59.8 (2)	C4—N3—C7—C8	−62.5 (2)
C6—N2—C2—C1	59.7 (2)	C5—N4—C8—C7	−63.3 (2)
C4—N2—C2—C1	−74.0 (2)	C6—N4—C8—C7	73.6 (2)
N1—C1—C2—N2	10.4 (3)	N3—C7—C8—N4	−9.0 (3)
C7—N3—C3—N1	−79.67 (19)	O11—C11—C12—C13	178.74 (17)
C4—N3—C3—N1	57.2 (2)	C16—C11—C12—C13	−1.2 (3)
C1—N1—C3—N3	−84.10 (19)	C11—C12—C13—C14	0.3 (3)
C5—N1—C3—N3	48.1 (2)	C11—C12—C13—C18	178.17 (17)
C3—N3—C4—N2	−51.5 (2)	C12—C13—C14—C15	1.1 (3)
C7—N3—C4—N2	85.2 (2)	C18—C13—C14—C15	−176.72 (17)
C2—N2—C4—N3	78.8 (2)	C12—C13—C14—Cl1	−178.85 (13)
C6—N2—C4—N3	−54.8 (2)	C18—C13—C14—Cl1	3.3 (2)
C6—N4—C5—N1	−51.7 (2)	C13—C14—C15—C16	−1.5 (2)
C8—N4—C5—N1	84.85 (19)	Cl1—C14—C15—C16	178.46 (13)
C1—N1—C5—N4	79.28 (19)	C13—C14—C15—C17	177.67 (16)
C3—N1—C5—N4	−53.1 (2)	Cl1—C14—C15—C17	−2.4 (2)
C2—N2—C6—N4	−83.3 (2)	O11—C11—C16—C15	−179.15 (17)
C4—N2—C6—N4	50.0 (2)	C12—C11—C16—C15	0.8 (3)
C5—N4—C6—N2	56.6 (2)	C14—C15—C16—C11	0.5 (3)
C8—N4—C6—N2	−80.1 (2)	C17—C15—C16—C11	−178.67 (17)

Hydrogen-bond geometry (Å, º)

Cg8 is the centroid of the C11–C16 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H11···N1	0.85 (4)	1.92 (4)	2.752 (2)	165 (3)
C3—H3*A*···*Cg*8^{i}	0.99	2.89	3.837 (2)	160
C8—H8*A*···*Cg*8^{ii}	0.99	2.88	3.814 (2)	157

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