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Crystal structure of the co-crystalline adduct 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD)–4-iodophenol (1/2): supramolecular assembly mediated by halogen and hydrogen bonding

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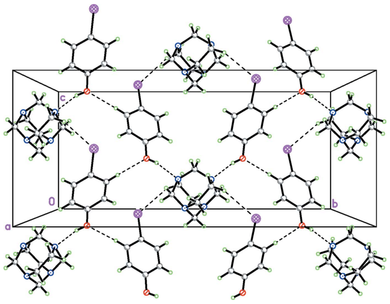
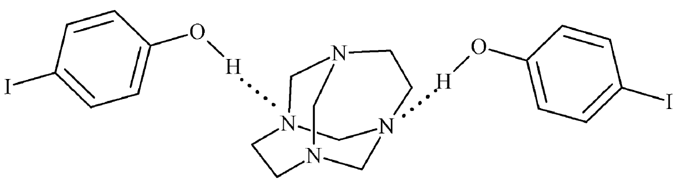
The asymmetric unit of the title co-crystalline adduct, 1,3,6,8-tetraazatricyclo-[4.4.1.1^{3,8}]dodecane (TATD)–4-iodophenol (1/2), $C_8H_{16}N_4 \cdot 2C_6H_5IO$, comprises a half molecule of the aminal cage polyamine plus a 4-iodophenol molecule. A twofold rotation axis generates the other half of the adduct. The components are linked by two intermolecular O—H···N hydrogen bonds. The adducts are further linked into a three-dimensional framework structure by a combination of N···I halogen bonds and weak non-conventional C—H···O and C—H···I hydrogen bonds.



1. Chemical context

Halogenoorganic compounds are able to play a role in organic supramolecular assemblies as electrophilic species, and have been used as models in the construction of self-assembled architectures. Non-covalent bonds such as hydrogen bonds (HB) and halogen bonds (XB) attract interest in crystal engineering because they have clear directional properties (Umezono & Okuno, 2017). Hydrogen bonds have been used successfully to construct supramolecular architectures as a result of their high directionality, which also results in high selectivity. Halogen bonds exhibit similar directionality and strength to hydrogen bonds and can offer a new approach to the control of supramolecular assemblies (Jin *et al.*, 2014). XB also play important roles in natural systems, and have been effectively applied in various fields including crystal engineering, solid-state molecular recognition, materials with optical properties and supramolecular liquid crystals (Li *et al.*, 2017). The strength of the interactions involving halogens increases on going from chlorine to bromine to iodine. Although hydrogen bonds are likely to be more effective, XB also are also important in crystal packing (Aakeröy *et al.*, 2015; Geboes *et al.*, 2017). In view of the analogies between halogen and hydrogen bonding, we think that the 4-iodophenol molecule offers interesting possibilities for exploring the effect of halogen-bonding interactions on supramolecular assemblies of phenols with polyamines. Following our previous work on acid–base adducts based on macrocyclic aminals and phenols, we report herein the synthesis and crystal structure of the title compound, a supramolecular complex assembled through non-covalent HB and XB interactions between 4-iodophenol and 1,3,6,8-tetraazatricyclo[4.4.1.13,8]dodecane (TATD).



2. Structural commentary

The title compound is isostructural with 1,3,6,8-tetraazatricyclo[4.4.1.$1^{3,8}$]dodecane (TATD)–4-bromophenol (Rivera, Uribe *et al.*, 2015): both crystallize in the space group *Fdd*2, and the differences between the unit-cell parameters (*a*, *b*, *c*) are < 7%. The asymmetric unit comprises one half of a 1,3,6,8-tetraazatricyclo[4.4.1.$1^{3,8}$]dodecane (TATD) molecule and one iodophenol molecule held together by intermolecular O—H···N hydrogen bonds [O···N 2.741 (6) Å; O—H···N 154 (7)°; Table 1]. The complete adduct is generated by a crystallographic twofold rotation axis, (Fig. 1).

Apart from the C—I/Br bond-length differences and some of the bond angles in the benzene ring, the molecules have similar geometric data (bond lengths and angles). The C14—I1 bond length [2.106 (5) Å] is in good agreement with the value reported for 4-iodophenol itself [2.104 (5) Å; Merz, 2006]. The overall molecular conformation of TATD observed here is very close to that of TATD in the related bromophenol adduct (Rivera, Uribe *et al.*, 2015).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.84 (1)	1.96 (4)	2.741 (6)	154 (7)
C5—H5*B*···I1^{i}	0.99	3.03	3.961 (7)	158
C13—H13···O1^{ii}	0.95	2.53	3.455 (6)	165

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

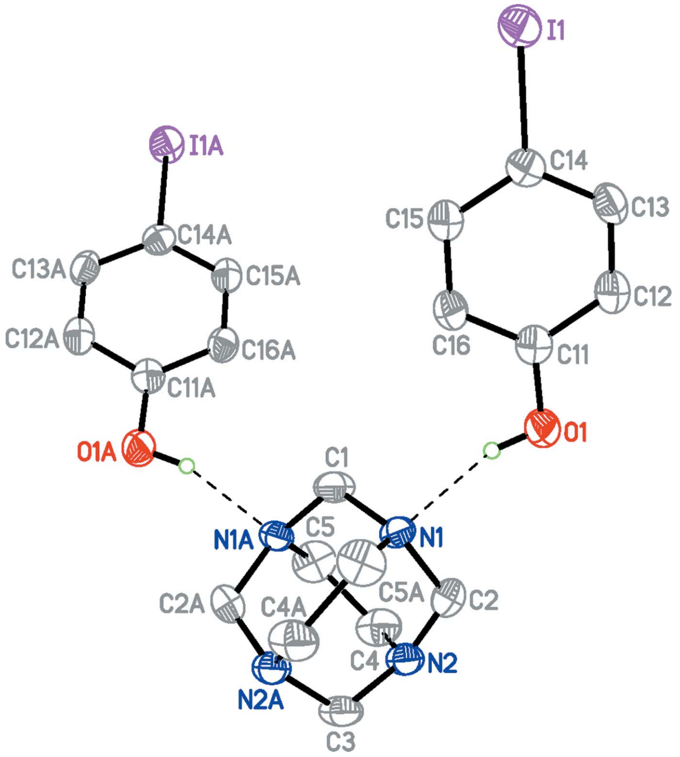


Figure 1
A view of the molecular structure of the title compound, showing the atom-labelling scheme, with displacement ellipsoids drawn at the 50% probability. H atoms bonded to C atoms are omitted for clarity. Hydrogen bonds are drawn as dashed lines. Atoms labelled with the suffix A are generated using the symmetry operator ($-x + 1$, $-y + 1$, z).

3. Supramolecular features

In the crystal, the three independent molecules are linked *via* two intermolecular O1—H1···N1 hydrogen bonds (Table 1 and Fig. 1). These supramolecular units are then linked by direction-specific intermolecular interactions, including both non-conventional hydrogen bonds and halogen bonds, C—H···O and C—H···I hydrogen bonds, forming slabs lying parallel to the *bc* plane (Table 1 and Fig. 2). However, considering the donor–acceptor bond lengths of 3.961 (7) Å [C5—H5*B*···I1] and 3.455 (6) Å [C13—H13···O1], which exceed the sum of the corresponding van der Waals radii (0.281 and 0.255 Å, respectively), the strength of the these non-conventional hydrogen bonds can be classified as very weak (Steiner, 2003).

In addition, as indicated by a *PLATON* analysis (Spek, 2009), the iodine atom is involved, as an electron-density acceptor, in two short contacts with N2 and C3, seemingly forming a bifurcated halogen bond, where the I···N [3.351 (5) Å] and I···C distances [3.519 (5) Å] are 0.18 and 0.16 Å, respectively, less than the sum of the corresponding

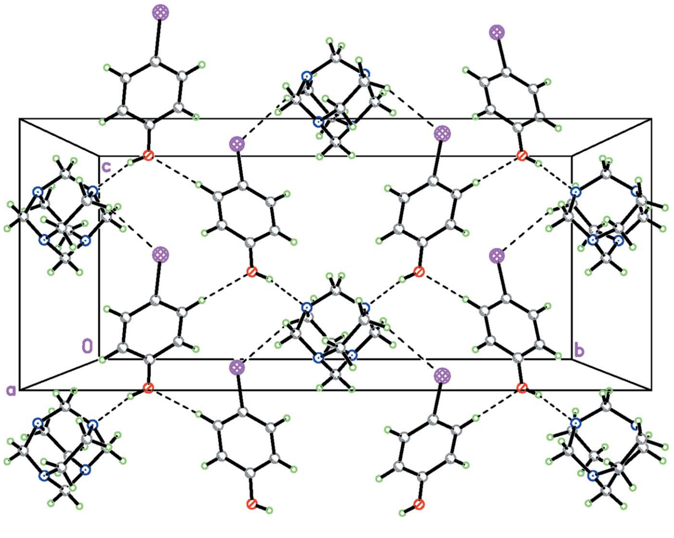


Figure 2
A view of the crystal packing of the title compound, showing the O—H···N hydrogen bonds; and C—H···O and C—H···hydrogen bonds (dashed lines).

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van der Waals radii (Alvarez, 2013). The I$\cdots$N distance corresponds to 90% of the sum of the van der Waals radii (3.70 Å) and the C14—I1$\cdots$N2^{iii} angle of 173.11 (2)° is close to being linear [symmetry code: (iii) $x + \frac{1}{4}, -y + \frac{5}{4}, z + \frac{5}{4}$]. Taking into account these geometrical parameters, the I1$\cdots$N2 contacts can formally be considered as halogen bonds. It appears that this contact imposes the relatively close, but significantly longer I$\cdots$C contact. Unsurprisingly, this pattern is repeated with the isostructural bromo analogue (Rivera, Uribe *et al.*, 2015) with Br$\cdots$N = 3.292 (4) and C$\cdots$Br = 3.477 (4) Å. There is also a Cl$\cdots$N halogen bond in the related 4-chloro-3,5-dimethylphenol analogue (Rivera, Rojas, *et al.*, 2015) with Cl$\cdots$N = 3.1680 (16); the C$\cdots$Cl contact has extended to 3.5828 (19) Å and can be disregarded.

4. Database survey

The structure of 1,3,6,8-tetraazatricyclo[4.4.1.13,8]dodecane has already been determined (Murray-Rust, 1974; Rivera *et al.*, 2014). Since the molecule is rigid, it is not surprising that it compares very closely with the TATD molecule in the title compound. The structure of 1,3,6,8-tetraazatricyclo-[4.4.1.13,8]dodecane hydroquinone (Rivera *et al.*, 2007) shows two O—H$\cdots$N hydrogen bonds of similar geometry to that of the title compound. Interestingly, this pattern is repeated with 4-bromophenol 1,3,6,8-tetraazatricyclo[4.4.1.13,8]dodecane (Rivera, Uribe *et al.*, 2015), which is isostructural with the title compound. In contrast, 4-chloro-3,5-dimethylphenol 1,3,6,8-tetraazatricyclo[4.4.1.13,8]dodecane (Rivera, Rojas *et al.*, 2015) only forms one O—H$\cdots$N hydrogen bond, nonetheless with similar geometric parameters to those in the title compound. Similarly, in the supramolecular complex with a 2:1 ratio of 4-iodophenol to the aza-donor 1,4-diazabicyclo-[2.2.2]octane (Nayak & Pedireddi, 2017), the molecules are again connected through O—H$\cdots$N hydrogen bonds but with no halogen-bond interaction involving the iodo substituent.

5. Synthesis and crystallization

A mixture of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD) (0.168g, 1 mmol) and 4-iodophenol (0.440g, 2 mmol) was ground at room temperature with a pestle in a mortar for 15 min., as required to complete the reaction (TLC). The mixture was recrystallized from a mixture of *n*-hexane with a few drops of ethanol to obtain crystals suitable for X-ray analysis, m.p. = 391 K. (yield: 56%).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were located in a difference electron-density map. The hydroxyl H atom was refined freely, while C-bound H atoms were fixed geometrically (C—H = 0.95 or 0.99 Å) and refined using a riding-model approximation, with U_{iso}(H) set to 1.2U_{eq} of the parent atom

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_8H_{16}N_4 \cdot 2C_6H_5IO$
M_r	608.25
Crystal system, space group	Orthorhombic, *Fdd*2
Temperature (K)	173
a, b, c (Å)	20.8869 (16), 22.4197 (13), 9.6352 (6)
V (Å^3)	4512.0 (5)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.81
Crystal size (mm)	0.24 × 0.23 × 0.23
Data collection	
Diffractometer	Stoe IPDS II two-circle
Absorption correction	Multi-scan (*X-AREA*; Stoe & Cie, 2001)
T_{min}, T_{max}	0.548, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7213, 2102, 2079
R_{int}	0.029
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.606
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.065, 1.06
No. of reflections	2102
No. of parameters	132
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.67
Absolute structure	Classical Flack (1983) method preferred over Parsons because s.u. lower
Absolute structure parameter	−0.03 (4)

Computer programs: *X-AREA* (Stoe & Cie, 2001), *XP* in *SHELXTL-Plus* and *SHELXS2016* (Sheldrick, 2008) and *SHELXL2016* (Sheldrick, 2015).

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supporting information

Acta Cryst. (2017). E**73**, 1692-1695 [https://doi.org/10.1107/S2056989017014943]

Crystal structure of the co-crystalline adduct 1,3,6,8-tetraazatricyclo-[4.4.1.1^{3,8}]dodecane (TATD)–4-iodophenol (1/2): supramolecular assembly mediated by halogen and hydrogen bonding

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: *SHELXS2016* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2016* (Sheldrick, 2015).

1,3,6,8-Tetraazatricyclo[4.4.1.1^{3,8}]dodecane–4-iodophenol (1/2)

Crystal data

$C_8H_{16}N_4 \cdot 2C_6H_5IO$
$M_r = 608.25$
Orthorhombic, *Fdd*2
$a = 20.8869$ (16) Å
$b = 22.4197$ (13) Å
$c = 9.6352$ (6) Å
$V = 4512.0$ (5) Å^3
$Z = 8$
$F(000) = 2368$
$D_x = 1.791$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 15571 reflections
$\theta = 3.6$–25.9°
$\mu = 2.81$ mm^{-1}
$T = 173$ K
Block, yellow
0.24 × 0.23 × 0.23 mm

Data collection

Stoe IPDS II two-circle diffractometer
Radiation source: Genix 3D IμS microfocus X-ray source
ω scans
Absorption correction: multi-scan (X-AREA; Stoe & Cie, 2001)
$T_{min} = 0.548$, $T_{max} = 1.000$
7213 measured reflections
2102 independent reflections
2079 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 25.5°$, $\theta_{min} = 3.6°$
$h = -24 \rightarrow 25$
$k = -26 \rightarrow 27$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.065$
$S = 1.06$
2102 reflections
132 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 5.1297P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Absolute structure: Classical Flack (1983) method preferred over Parsons because s.u. lower
Absolute structure parameter: −0.03 (4)

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 (Å^2)

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
N1	0.5189 (2)	0.55327 (17)	0.2785 (4)	0.0293 (9)	
N2	0.4501 (2)	0.5309 (2)	0.0695 (5)	0.0335 (9)	
C1	0.500000	0.500000	0.3551 (8)	0.0350 (16)	
H1A	0.463825	0.511142	0.416230	0.042*	0.5
H1B	0.536176	0.488858	0.416229	0.042*	0.5
C2	0.4734 (3)	0.5730 (3)	0.1705 (6)	0.0413 (13)	
H2A	0.435585	0.589927	0.218543	0.050*	
H2B	0.493847	0.606119	0.119081	0.050*	
C3	0.500000	0.500000	−0.0073 (9)	0.0383 (16)	
H3A	0.521109	0.529565	−0.068331	0.046*	0.5
H3B	0.478891	0.470437	−0.068336	0.046*	0.5
C4	0.3977 (3)	0.4922 (3)	0.1176 (7)	0.0439 (13)	
H4A	0.381691	0.469170	0.037109	0.053*	
H4B	0.362214	0.517973	0.149924	0.053*	
C5	0.4138 (3)	0.4485 (3)	0.2331 (7)	0.0456 (14)	
H5A	0.386853	0.458252	0.314539	0.055*	
H5B	0.401546	0.407971	0.201822	0.055*	
I1	0.63999 (2)	0.68958 (2)	1.00445 (6)	0.03902 (14)	
O1	0.5030 (2)	0.65445 (17)	0.4344 (4)	0.0364 (8)	
H1	0.518 (3)	0.623 (2)	0.402 (7)	0.05 (2)*	
C11	0.5320 (2)	0.6593 (2)	0.5604 (6)	0.0293 (10)	
C12	0.5220 (3)	0.7116 (2)	0.6361 (6)	0.0352 (11)	
H12	0.494289	0.741464	0.600328	0.042*	
C13	0.5518 (2)	0.72031 (19)	0.7624 (7)	0.0330 (10)	
H13	0.544963	0.756109	0.813067	0.040*	
C14	0.5920 (2)	0.6759 (2)	0.8149 (6)	0.0293 (10)	
C15	0.6015 (2)	0.6234 (2)	0.7428 (7)	0.0312 (9)	
H15	0.628314	0.593158	0.780345	0.037*	
C16	0.5715 (2)	0.6147 (2)	0.6143 (6)	0.0309 (10)	
H16	0.578032	0.578773	0.564169	0.037*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.038 (2)	0.028 (2)	0.022 (2)	−0.0009 (16)	−0.0024 (17)	0.0024 (16)

N2	0.031 (2)	0.045 (2)	0.025 (2)	0.0090 (19)	0.0002 (17)	0.0008 (18)
C1	0.047 (4)	0.035 (4)	0.023 (3)	−0.008 (3)	0.000	0.000
C2	0.050 (3)	0.038 (3)	0.036 (3)	0.015 (3)	−0.006 (2)	0.004 (2)
C3	0.032 (3)	0.061 (4)	0.022 (3)	0.011 (3)	0.000	0.000
C4	0.026 (2)	0.067 (4)	0.038 (3)	0.007 (2)	−0.003 (2)	0.002 (3)
C5	0.039 (3)	0.050 (3)	0.048 (4)	−0.007 (2)	−0.001 (3)	0.002 (3)
I1	0.0425 (2)	0.03403 (19)	0.0405 (2)	−0.00169 (13)	−0.00853 (15)	−0.00435 (16)
O1	0.044 (2)	0.0297 (18)	0.0355 (19)	0.0035 (16)	−0.0077 (17)	−0.0043 (16)
C11	0.024 (2)	0.030 (2)	0.034 (2)	−0.0028 (18)	0.0035 (19)	0.0018 (19)
C12	0.035 (3)	0.029 (2)	0.041 (3)	0.005 (2)	0.001 (2)	0.000 (2)
C13	0.037 (2)	0.0255 (19)	0.036 (3)	0.0028 (18)	0.007 (2)	−0.005 (3)
C14	0.027 (2)	0.032 (2)	0.030 (2)	−0.0029 (19)	0.003 (2)	0.000 (2)
C15	0.030 (2)	0.027 (2)	0.036 (3)	0.0023 (16)	0.001 (2)	0.001 (2)
C16	0.033 (2)	0.024 (2)	0.036 (2)	−0.0012 (18)	0.002 (2)	−0.002 (2)

Geometric parameters (Å, º)

N1—C1	1.458 (5)	C5—H5A	0.9900
N1—C5^{i}	1.474 (7)	C5—H5B	0.9900
N1—C2	1.478 (7)	I1—C14	2.106 (5)
N2—C2	1.440 (8)	O1—C11	1.361 (6)
N2—C3	1.453 (6)	O1—H1	0.838 (14)
N2—C4	1.472 (8)	C11—C16	1.395 (7)
C1—H1A	0.9900	C11—C12	1.397 (8)
C1—H1B	0.9900	C12—C13	1.381 (9)
C2—H2A	0.9900	C12—H12	0.9500
C2—H2B	0.9900	C13—C14	1.398 (8)
C3—H3A	0.9900	C13—H13	0.9500
C3—H3B	0.9900	C14—C15	1.382 (7)
C4—C5	1.520 (9)	C15—C16	1.401 (8)
C4—H4A	0.9900	C15—H15	0.9500
C4—H4B	0.9900	C16—H16	0.9500

C1—N1—C5^{i}	112.8 (4)	C5—C4—H4B	108.2
C1—N1—C2	115.3 (4)	H4A—C4—H4B	107.3
C5^{i}—N1—C2	114.4 (5)	N1^{i}—C5—C4	116.4 (5)
C2—N2—C3	114.5 (4)	N1^{i}—C5—H5A	108.2
C2—N2—C4	115.1 (5)	C4—C5—H5A	108.2
C3—N2—C4	114.4 (4)	N1^{i}—C5—H5B	108.2
N1—C1—N1^{i}	119.2 (6)	C4—C5—H5B	108.2
N1—C1—H1A	107.5	H5A—C5—H5B	107.3
N1^{i}—C1—H1A	107.5	C11—O1—H1	103 (5)
N1—C1—H1B	107.5	O1—C11—C16	122.6 (5)
N1^{i}—C1—H1B	107.5	O1—C11—C12	117.7 (5)
H1A—C1—H1B	107.0	C16—C11—C12	119.6 (5)
N2—C2—N1	119.8 (4)	C13—C12—C11	120.8 (5)
N2—C2—H2A	107.4	C13—C12—H12	119.6
N1—C2—H2A	107.4	C11—C12—H12	119.6

N2—C2—H2B	107.4	C12—C13—C14	119.3 (5)
N1—C2—H2B	107.4	C12—C13—H13	120.4
H2A—C2—H2B	106.9	C14—C13—H13	120.4
N2—C3—N2^{i}	118.8 (7)	C15—C14—C13	120.8 (5)
N2—C3—H3A	107.6	C15—C14—I1	119.5 (4)
N2^{i}—C3—H3A	107.6	C13—C14—I1	119.8 (4)
N2—C3—H3B	107.6	C14—C15—C16	119.8 (5)
N2^{i}—C3—H3B	107.6	C14—C15—H15	120.1
H3A—C3—H3B	107.0	C16—C15—H15	120.1
N2—C4—C5	116.5 (5)	C11—C16—C15	119.7 (5)
N2—C4—H4A	108.2	C11—C16—H16	120.2
C5—C4—H4A	108.2	C15—C16—H16	120.2
N2—C4—H4B	108.2		

C5^{i}—N1—C1—N1^{i}	−82.7 (4)	O1—C11—C12—C13	−177.7 (5)
C2—N1—C1—N1^{i}	51.3 (3)	C16—C11—C12—C13	1.5 (8)
C3—N2—C2—N1	−55.1 (7)	C11—C12—C13—C14	−0.5 (8)
C4—N2—C2—N1	80.5 (7)	C12—C13—C14—C15	−0.9 (8)
C1—N1—C2—N2	−50.6 (7)	C12—C13—C14—I1	178.2 (4)
C5^{i}—N1—C2—N2	82.6 (7)	C13—C14—C15—C16	1.3 (8)
C2—N2—C3—N2^{i}	53.6 (4)	I1—C14—C15—C16	−177.8 (4)
C4—N2—C3—N2^{i}	−82.3 (4)	O1—C11—C16—C15	178.1 (5)
C2—N2—C4—C5	−65.6 (7)	C12—C11—C16—C15	−1.1 (8)
C3—N2—C4—C5	70.1 (7)	C14—C15—C16—C11	−0.3 (8)
N2—C4—C5—N1^{i}	−3.8 (8)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.84 (1)	1.96 (4)	2.741 (6)	154 (7)
C5—H5*B*···I1^{ii}	0.99	3.03	3.961 (7)	158
C13—H13···O1^{iii}	0.95	2.53	3.455 (6)	165

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