

Crystal structure of the co-crystalline adduct
1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane
(TATD)–4-bromophenol (1/2)Augusto Rivera,^{a*} Juan Manuel Uribe,^a Jicli José Rojas,^a Jaime Ríos-Motta^a and Michael Bolte^b

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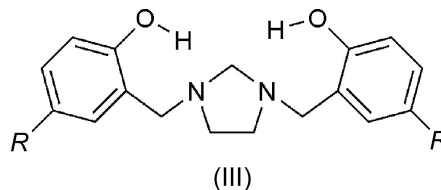
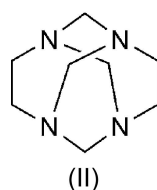
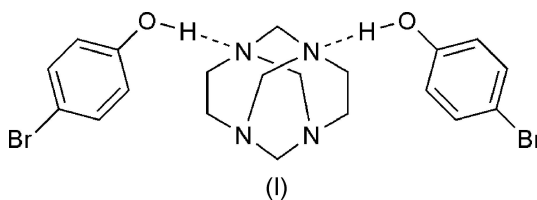
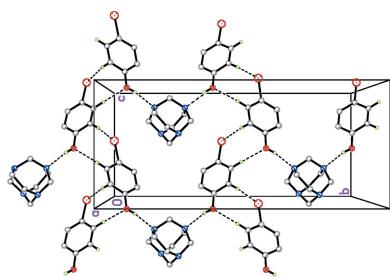
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Keywords: crystal structure; co-crystalline adducts; TATD; proton transfer; hydrogen bonding**CCDC reference:** 1057775**Supporting information:** this article has supporting information at journals.iucr.org/e^aUniversidad Nacional de Colombia, Sede Bogotá, Facultad de Ciencias, Departamento de Química, Cra 30 No. 45-03, Bogotá, Código Postal 111321, Colombia, and ^bInstitut für Anorganische Chemie, J. W. Goethe-Universität Frankfurt, Max-von-Laue-Strasse 7, 60438 Frankfurt/Main, Germany. *Correspondence e-mail: ariverau@unal.edu.co

The structure of the 1:2 co-crystalline adduct C₈H₁₆N₄·2C₆H₅BrO, (I), from the solid-state reaction of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD) and 4-bromophenol, has been determined. The asymmetric unit of the title co-crystalline adduct comprises a half molecule of a minimal cage polyamine plus a 4-bromophenol molecule. A twofold rotation axis generates the other half of the adduct. The primary inter-species association in the title compound is through two intermolecular O–H···N hydrogen bonds. In the crystal, the adducts are linked by weak non-conventional C–H···O and C–H···Br hydrogen bonds, giving a two-dimensional supramolecular structure parallel to the *bc* plane.

1. Chemical context

The main focus of the research in our laboratory is the synthesis of a variety of molecules using cyclic aminals of the adamantane type. The prototype of these reactions is a Mannich-type reaction involving 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD) (II) with phenols which, in solution, affords di-Mannich bases of type (III) (Rivera *et al.*, 1993, 2005). These are common systems for the investigation of hydrogen bonding and proton transfer. Engaged in the development of greener synthetic pathways, we attempted a synthesis of a di-Mannich base under solvent-free conditions by simply grinding TATD and 4-bromophenol at room temperature without using any solvent in the initial step. We found that the reaction did not provide the di-Mannich base as desired. Instead, the title compound, (I), was obtained in good yield. The reaction is run in the absence of solvent, there are no by-products, and the work-up procedure is easy. Recrystallization in an appropriate solvent gave the title compound in high yield.



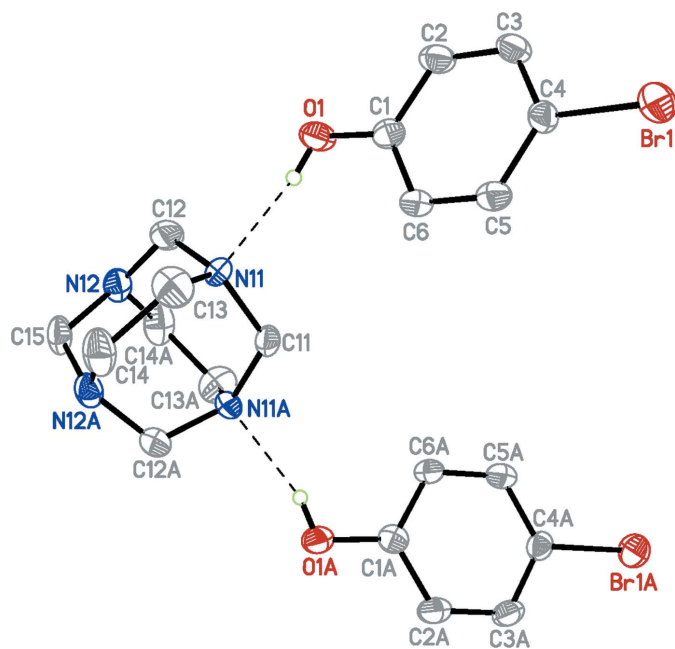


Figure 1
The molecular structure of the title adduct. Displacement ellipsoids are drawn at the 50% probability level. H atoms bonded to C atoms are omitted for clarity. Hydrogen bonds are drawn as dashed lines. Atoms labelled with the suffix A are generated using the symmetry operator $(-x - \frac{1}{2}, -y - \frac{1}{2}, z)$.

2. Structural commentary

Co-crystal (I) crystallized in the space group $Fdd2$ with one half-molecule of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD) and one molecule of 4-bromophenol in the asymmetric unit; a twofold rotation axis generates the other half of the adduct held together by two intermolecular O—H \cdots N hydrogen bonds [O \cdots N 2.705 (5) Å; O—H \cdots N 158 (7) $^\circ$] (Fig. 1). Unlike the situation in a related structure (Rivera *et al.*, (2007), where a 1:1 adduct formed *via* an O—H \cdots N

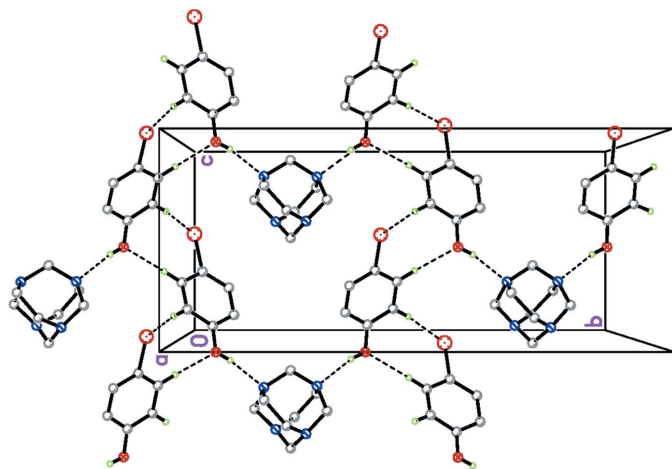


Figure 2
The crystal packing of the title compound, showing two of the chains that extend along the crystal c -axis direction. C—H \cdots O and C—H \cdots Br hydrogen bonds are drawn as dashed lines.

Table 1
Hydrogen-bond geometry (Å, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots N11	0.78 (7)	1.97 (7)	2.705 (5)	158 (7)
C3—H3 \cdots O1 ⁱ	0.95	2.42	3.347 (6)	164
C13—H13A \cdots Br1 ⁱⁱ	0.99	2.89	3.833 (6)	159

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

hydrogen bond between TATD and hydroquinone, the title compound features a 1:2 adduct. Bond lengths in the TATD and 4-bromophenol molecules in (I) are within normal ranges (Allen *et al.*, 1987) and are comparable to those found in similar structures (Rivera *et al.*, 2007; Tse *et al.*, 1977). The H atom of the phenolic —OH group deviates slightly from the benzene ring plane, subtending a torsion angle of 8(5) $^\circ$.

A significant reduction in the O \cdots N distance is observed when the distance and angle in the O1—H1 \cdots N1 hydrogen bond [O \cdots N 2.705 (5) Å; O—H \cdots N 158 (7) $^\circ$] in the title compound are compared to the values found in the TATD:hydroquinone, 1:1 adduct [O \cdots N 2.767 (2) Å; O—H \cdots N 156.3 (10) $^\circ$] (Rivera *et al.*, 2007). Also, the C1—O1 bond length observed here [1.355 (6) Å], is shorter than that in the hydroquinone co-crystal. This indicates an increase in hydrogen-bonding strength in the title compound, which may be due to the considerable differences in the pK_a values between the species involved in the hydrogen bond (Majerz *et al.*, 1997). Compared to hydroquinone ($pK_a = 9.85$), p -bromophenol is more acidic ($pK_a = 9.37$) (Lide, 2003).

3. Supramolecular features

In the crystal of the title compound, the adducts are weakly linked peripherally through both non-conventional C—H \cdots O and C—H \cdots Br hydrogen bonds (Table 1) giving a two dimensional supramolecular structure parallel to the bc plane. (Fig. 2). This is similar to the structure of the 4-bromophenol adduct with urotropine (Tse *et al.*, 1977).

4. Database survey

A database search (CSD version 5.36, November 2014 plus two updates) for 4-bromophenol yielded 17 hits with 21 fragments. The mean C—O bond length in these structures is 1.35 (5) Å and the mean C—Br bond length is 1.91 (3) Å. These values are in excellent agreement with those of the title compound, *i.e.* O1—C1 1.355 (6) and Br1—C4 1.907 (5) Å.

A database search for 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane yielded only three hits, two determinations of the compound itself (Murray-Rust, 1974; Rivera *et al.*, 2014) and a co-crystal of the aminal with hydroquinone (Rivera *et al.*, 2007). While the molecules of 1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane itself have $\bar{4}2m$ symmetry, the molecules in the co-crystal of TATD with hydroquinone have mirror symmetry. In the title compound, on the other hand, the

Table 2
Experimental details.

Crystal data	
Chemical formula	C ₈ H ₁₆ N ₄ ·2C ₆ H ₅ BrO
<i>M</i> _r	514.27
Crystal system, space group	Orthorhombic, <i>Fdd2</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	20.693 (2), 21.7954 (18), 9.4649 (9)
<i>V</i> (Å ³)	4268.8 (7)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm ⁻¹)	3.82
Crystal size (mm)	0.29 × 0.27 × 0.23
Data collection	
Diffractometer	Stoe <i>IPDS</i> II two-circle
Absorption correction	Multi-scan (<i>MULABS</i> ; Spek, 2009; Blessing, 1995)
<i>T</i> _{min} , <i>T</i> _{max}	0.847, 0.972
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	5997, 1996, 1833
<i>R</i> _{int}	0.062
(sin θ/ <i>λ</i>) _{max} (Å ⁻¹)	0.608
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.032, 0.069, 1.01
No. of reflections	1996
No. of parameters	132
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δ <i>ρ</i> _{max} , Δ <i>ρ</i> _{min} (e Å ⁻³)	0.24, -0.41
Absolute structure	Flack <i>x</i> determined using 792 quotients [(<i>I</i> ⁺) - (<i>I</i> ⁻)] / [(<i>I</i> ⁺) + (<i>I</i> ⁻)] (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.003 (16)

Computer programs: *X-AREA* (Stoe & Cie, 2001), *SHELXS97* and *XP* in *SHELXL-Plus* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *Mercury* (Macrae *et al.*, 2006).

1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane molecule displays C₂ symmetry.

5. Synthesis and crystallization

1,3,6,8-tetraazatricyclo[4.4.1.1^{3,8}]dodecane (TATD) (0.21 g, 1.25 mmol) and 4-bromophenol (0.43 g, 2.5 mmol) were manually mixed in a mortar with pestle at room temperature for 20 min as required to complete the reaction (TLC). The mixture was then dissolved in a minimum amount of methanol

and left to crystallize at room temperature. Subsequent recrystallization with MeOH then yielded the title compound as white crystals in 78% yield, m.p. = 367–368 K.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. All the 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 1.2*U*_{eq} of the parent atom.

Acknowledgements

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supporting information

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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-bromophenol (1/2)

Augusto Rivera, Juan Manuel Uribe, 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) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

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

Crystal data

$C_8H_{16}N_4 \cdot 2C_6H_5BrO$

$M_r = 514.27$

Orthorhombic, *Fdd2*

$a = 20.693$ (2) Å

$b = 21.7954$ (18) Å

$c = 9.4649$ (9) Å

$V = 4268.8$ (7) Å³

$Z = 8$

$F(000) = 2080$

$D_x = 1.600$ Mg m⁻³

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

Cell parameters from 7202 reflections

$\theta = 3.7$ – 26.0°

$\mu = 3.82$ mm⁻¹

$T = 173$ K

Block, colourless

$0.29 \times 0.27 \times 0.23$ 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 (MULABS; Spek, 2009; Blessing, 1995)

$T_{\min} = 0.847$, $T_{\max} = 0.972$

5997 measured reflections

1996 independent reflections

1833 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.062$

$\theta_{\max} = 25.6^\circ$, $\theta_{\min} = 3.7^\circ$

$h = -22 \rightarrow 24$

$k = -25 \rightarrow 26$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.069$

$S = 1.01$

1996 reflections

132 parameters

1 restraint

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2]$

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

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

$\Delta\rho_{\max} = 0.24$ e Å⁻³

$\Delta\rho_{\min} = -0.41$ e Å⁻³

Absolute structure: Flack x determined using

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

Absolute structure parameter: 0.003 (16)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Br1	-0.11272 (3)	-0.43922 (2)	1.02771 (5)	0.03734 (18)	
O1	-0.2465 (2)	-0.40437 (17)	0.4684 (4)	0.0311 (9)	
H1	-0.233 (4)	-0.375 (3)	0.432 (7)	0.036 (18)*	
C1	-0.2172 (3)	-0.4091 (2)	0.5959 (5)	0.0232 (11)	
C2	-0.2281 (3)	-0.4622 (2)	0.6734 (6)	0.0288 (12)	
H2	-0.2567	-0.4926	0.6379	0.035*	
C3	-0.1978 (3)	-0.4710 (2)	0.8016 (5)	0.0281 (11)	
H3	-0.2048	-0.5077	0.8536	0.034*	
C4	-0.1570 (3)	-0.4262 (2)	0.8536 (5)	0.0246 (10)	
C5	-0.1468 (2)	-0.37234 (18)	0.7795 (7)	0.0252 (10)	
H5	-0.1190	-0.3416	0.8165	0.030*	
C6	-0.1773 (3)	-0.3635 (2)	0.6514 (5)	0.0257 (11)	
H6	-0.1711	-0.3263	0.6009	0.031*	
N11	-0.2299 (2)	-0.30437 (16)	0.3032 (4)	0.0241 (9)	
N12	-0.2997 (2)	-0.2824 (2)	0.0903 (4)	0.0276 (10)	
C11	-0.2500	-0.2500	0.3809 (7)	0.0278 (16)	
H11A	-0.2137	-0.2379	0.4431	0.033*	0.5
H11B	-0.2863	-0.2621	0.4431	0.033*	0.5
C12	-0.2756 (3)	-0.3255 (2)	0.1929 (6)	0.0354 (14)	
H12A	-0.2542	-0.3592	0.1404	0.042*	
H12B	-0.3134	-0.3436	0.2416	0.042*	
C13	-0.1623 (3)	-0.3018 (2)	0.2559 (7)	0.0398 (14)	
H13A	-0.1497	-0.3431	0.2227	0.048*	
H13B	-0.1349	-0.2919	0.3386	0.048*	
C14	-0.1470 (3)	-0.2560 (3)	0.1394 (6)	0.0389 (13)	
H14A	-0.1120	-0.2287	0.1734	0.047*	
H14B	-0.1298	-0.2790	0.0574	0.047*	
C15	-0.2500	-0.2500	0.0114 (7)	0.0314 (16)	
H15A	-0.2282	-0.2801	-0.0507	0.038*	0.5
H15B	-0.2718	-0.2199	-0.0507	0.038*	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0464 (3)	0.0333 (2)	0.0323 (2)	0.0043 (3)	-0.0102 (3)	0.0045 (2)
O1	0.039 (3)	0.0219 (18)	0.0323 (19)	-0.0044 (18)	-0.0097 (17)	0.0049 (15)
C1	0.021 (3)	0.022 (2)	0.027 (2)	0.004 (2)	0.001 (2)	-0.0017 (19)
C2	0.032 (3)	0.020 (2)	0.034 (3)	-0.003 (2)	0.003 (2)	0.001 (2)
C3	0.034 (3)	0.020 (2)	0.030 (3)	-0.001 (2)	0.005 (2)	0.005 (2)

C4	0.029 (3)	0.024 (2)	0.021 (2)	0.004 (2)	0.004 (2)	0.0013 (18)
C5	0.026 (3)	0.0200 (18)	0.030 (2)	-0.0030 (18)	0.001 (3)	-0.002 (3)
C6	0.033 (3)	0.018 (2)	0.027 (2)	-0.003 (2)	0.002 (2)	0.0007 (18)
N11	0.032 (2)	0.0210 (18)	0.019 (2)	-0.0012 (17)	0.0013 (17)	-0.0048 (15)
N12	0.025 (2)	0.036 (2)	0.0222 (19)	-0.009 (2)	-0.0016 (18)	-0.0016 (17)
C11	0.043 (5)	0.024 (3)	0.016 (3)	0.005 (3)	0.000	0.000
C12	0.050 (4)	0.027 (3)	0.029 (3)	-0.014 (3)	-0.006 (2)	-0.001 (2)
C13	0.034 (3)	0.041 (3)	0.045 (4)	0.006 (2)	0.002 (3)	0.004 (3)
C14	0.027 (3)	0.061 (4)	0.029 (3)	-0.006 (3)	0.003 (2)	0.001 (3)
C15	0.034 (4)	0.046 (4)	0.015 (3)	-0.006 (3)	0.000	0.000

Geometric parameters (Å, °)

Br1—C4	1.907 (5)	N12—C15	1.453 (6)
O1—C1	1.355 (6)	N12—C14 ⁱ	1.462 (8)
O1—H1	0.78 (7)	C11—N11 ⁱ	1.456 (5)
C1—C2	1.388 (7)	C11—H11A	0.9900
C1—C6	1.393 (7)	C11—H11B	0.9900
C2—C3	1.380 (8)	C12—H12A	0.9900
C2—H2	0.9500	C12—H12B	0.9900
C3—C4	1.381 (7)	C13—C14	1.520 (8)
C3—H3	0.9500	C13—H13A	0.9900
C4—C5	1.384 (7)	C13—H13B	0.9900
C5—C6	1.380 (8)	C14—N12 ⁱ	1.462 (8)
C5—H5	0.9500	C14—H14A	0.9900
C6—H6	0.9500	C14—H14B	0.9900
N11—C11	1.456 (5)	C15—N12 ⁱ	1.453 (6)
N11—C13	1.470 (8)	C15—H15A	0.9900
N11—C12	1.482 (7)	C15—H15B	0.9900
N12—C12	1.441 (7)		
C1—O1—H1	107 (5)	N11—C11—H11B	107.5
O1—C1—C2	117.4 (5)	N11 ⁱ —C11—H11B	107.5
O1—C1—C6	123.1 (5)	H11A—C11—H11B	107.0
C2—C1—C6	119.5 (5)	N12—C12—N11	119.5 (4)
C3—C2—C1	120.4 (5)	N12—C12—H12A	107.4
C3—C2—H2	119.8	N11—C12—H12A	107.4
C1—C2—H2	119.8	N12—C12—H12B	107.4
C2—C3—C4	119.6 (4)	N11—C12—H12B	107.4
C2—C3—H3	120.2	H12A—C12—H12B	107.0
C4—C3—H3	120.2	N11—C13—C14	116.4 (5)
C3—C4—C5	120.8 (5)	N11—C13—H13A	108.2
C3—C4—Br1	119.8 (4)	C14—C13—H13A	108.2
C5—C4—Br1	119.4 (4)	N11—C13—H13B	108.2
C6—C5—C4	119.6 (4)	C14—C13—H13B	108.2
C6—C5—H5	120.2	H13A—C13—H13B	107.3
C4—C5—H5	120.2	N12 ⁱ —C14—C13	116.6 (5)
C5—C6—C1	120.1 (4)	N12 ⁱ —C14—H14A	108.1

C5—C6—H6	119.9	C13—C14—H14A	108.1
C1—C6—H6	119.9	N12 ⁱ —C14—H14B	108.1
C11—N11—C13	113.2 (3)	C13—C14—H14B	108.1
C11—N11—C12	115.3 (4)	H14A—C14—H14B	107.3
C13—N11—C12	113.9 (4)	N12 ⁱ —C15—N12	118.2 (6)
C12—N12—C15	114.7 (4)	N12 ⁱ —C15—H15A	107.8
C12—N12—C14 ⁱ	114.9 (4)	N12—C15—H15A	107.8
C15—N12—C14 ⁱ	114.8 (4)	N12 ⁱ —C15—H15B	107.8
N11—C11—N11 ⁱ	119.3 (5)	N12—C15—H15B	107.8
N11—C11—H11A	107.5	H15A—C15—H15B	107.1
N11 ⁱ —C11—H11A	107.5		
O1—C1—C2—C3	177.5 (5)	C12—N11—C11—N11 ⁱ	-51.2 (3)
C6—C1—C2—C3	-2.7 (8)	C15—N12—C12—N11	55.6 (7)
C1—C2—C3—C4	1.0 (8)	C14 ⁱ —N12—C12—N11	-80.7 (7)
C2—C3—C4—C5	0.7 (8)	C11—N11—C12—N12	50.6 (7)
C2—C3—C4—Br1	-178.0 (4)	C13—N11—C12—N12	-82.8 (6)
C3—C4—C5—C6	-0.6 (8)	C11—N11—C13—C14	-69.9 (6)
Br1—C4—C5—C6	178.1 (4)	C12—N11—C13—C14	64.4 (6)
C4—C5—C6—C1	-1.2 (8)	N11—C13—C14—N12 ⁱ	2.4 (7)
O1—C1—C6—C5	-177.4 (5)	C12—N12—C15—N12 ⁱ	-53.9 (3)
C2—C1—C6—C5	2.8 (8)	C14 ⁱ —N12—C15—N12 ⁱ	82.4 (4)
C13—N11—C11—N11 ⁱ	82.4 (4)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 ⁱⁱⁱ —N11	0.78 (7)	1.97 (7)	2.705 (5)	158 (7)
C3—H3 ⁱⁱⁱ —O1 ⁱⁱ	0.95	2.42	3.347 (6)	164
C13—H13A ⁱⁱⁱ —Br1 ⁱⁱⁱ	0.99	2.89	3.833 (6)	159

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