

# First hydrogen-bonded adduct of sterically hindered 2-*tert*-butyl-4-methylphenol (TBMP) with 1,3,6,8-tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane (TATD) *via* coupling of classical hydrogen bonds and C—H··· $\pi$ non-covalent interactions

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Received 10 March 2022

Accepted 9 May 2022

Edited by C. Schulzke, Universität Greifswald, Germany

**Keywords:** crystal structure; co-crystalline adduct; hydrogen bonding; C—H··· $\pi$  interactions; TBMP; TATD.

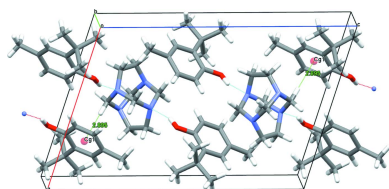
**CCDC reference:** 2092229

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

The title compound, C<sub>8</sub>H<sub>16</sub>N<sub>4</sub>·2C<sub>11</sub>H<sub>16</sub>O, was synthesized from the corresponding sterically crowded phenol by treatment with the aminal cage polyamine. Single-crystal X-ray diffraction structural analysis revealed the three-molecule aggregate to crystallize in the monoclinic space group *P2*/*c* with one half of a 1,3,6,8-tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane (TATD) molecule and one 2-*tert*-butyl-4-methylphenol molecule per asymmetric unit. The crystal structure features intermolecular O—H···N and C—H···O hydrogen bonds, as well as intermolecular C—H··· $\pi$  interactions.

## 1. Chemical context

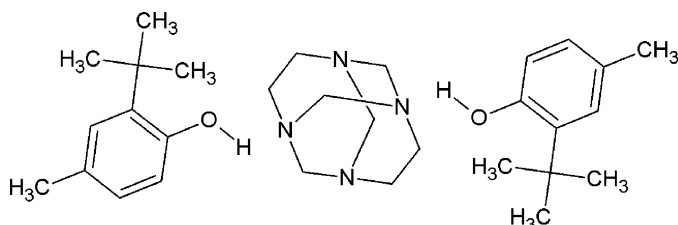
Co-crystals of phenols with various nitrogen bases are model systems often used for studying the nature of the hydrogen bond (Majerz *et al.*, 2007). In this context, not only the initial formation of a hydrogen-bonded adduct was investigated between a Mannich preformed reagent and the phenolic substrate (Burckhalter & Leib, 1961), but also the great interest in and chemical importance of the aminoalkylation of aromatic substrates *via* the Mannich reaction was addressed (Tramontini *et al.*, 1988). For a long time we have directed continuing efforts to the systematic study of hydrogen bonding and other non-covalent interactions of phenols with aminal cages (preformed Mannich bases) (Rivera *et al.*, 2007, 2015*a,b*, 2017*a,b*, 2019). Herein we report the mechanochemical preparation and crystal structure of the title adduct prepared by mixing in an agate mortar the sterically hindered 2-*tert*-butyl-4-methylphenol (TBMP) with 1,3,6,8-tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane (TATD) in a 2:1 ratio. The crystallographic information available for pure 2-*tert*-butyl-4-methylphenol (Beckmann *et al.*, 2004) does not report O—H···O hydrogen bonds, which are commonly found in the crystal structures of alcohols, suggesting that the alcohol is sterically protected. The reaction of TBMP with TATD, in notable contrast to this, proceeds cleanly to give the title O—H···N hydrogen-bonded adduct exclusively. A search of the Cambridge Structural Database (version 5.42; Groom *et al.*, 2016) for crystal structures containing hydrogen-bonded TBMP co-crystals with a hydrogen-bond acceptor resulted in zero hits, emphasizing the general rarity of this observation.



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The resultant crystal structure reported here also exhibits C—H···O hydrogen-bonding interactions, which constitute a fundamental force in maintaining crystal and three-dimensional chemical structures in chemistry and biology (Wang *et al.*, 2019).



## 2. Structural commentary

The title compound crystallizes in the monoclinic space group  $P2_1/c$ . The asymmetric unit comprises one half of a 1,3,6,8-tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane (TATD) molecule and one 2-*tert*-butyl-4-methylphenol (TBMP) molecule held together by one intermolecular O—H···N hydrogen bond [ $O\cdots N = 2.8534(15)$  Å;  $O-H\cdots N = 161.6(17)^\circ$ ; Table 1]. The complete adduct is generated by symmetry by a crystallographic twofold rotation axis, resulting in  $C_2$  symmetry for the three-molecule aggregate (Fig. 1). Apart from the two neutral intermolecular O—H···N bonds in the three-molecule arrangement, as indicated by a *PLATON* analysis (Spek, 2020), there are four non-classical intramolecular C—H···O hydrogen bonds between the TBMP phenol oxygen atoms and the *ortho tert*-butyl C—H bonds (two for each phenol oxygen atom O1; methyl group atoms C18—H18*B* and C20—H20*A*; geometric details are given in Table 1).

The —OH group is not perfectly co-planar with the benzene ring with a C16—C11—O1—H1 torsion angle of  $18.0^\circ$ . This angle differs from the corresponding more acute torsion angles in free 2-*tert*-butyl-4-methylphenol ( $0.73$  and  $-0.36^\circ$ ; Beckmann *et al.*, 2004) and other related sterically very congested phenols (Lutz & Spek, 2005). The observed C11—O1 bond length [ $1.376(2)$  Å] is in a good agreement with the mean value of  $1.377$  Å reported for 2-*tert*-butyl-4-methylphenol (Beckmann *et al.*, 2004).

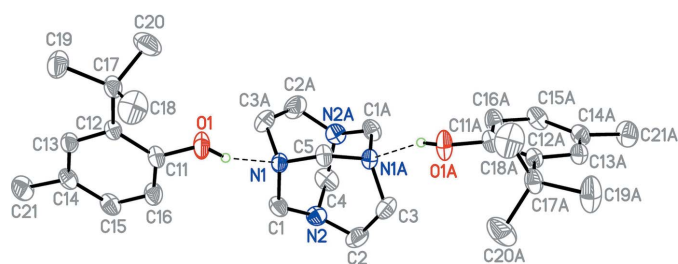


Figure 1

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

Table 1

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C11—C16 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···N1	0.88 (2)	2.01 (2)	2.8534 (15)	161.6 (17)
C18—H18 <i>B</i> ···O1	0.98	2.30	2.966 (2)	124
C20—H20 <i>A</i> ···O1	0.98	2.41	3.058 (3)	124
C1—H1 <i>A</i> ···Cg1 <sup>1</sup>	0.98	2.90	3.851 (2)	163

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

The C—N1 bond lengths of the nitrogen atom, which is engaged in the intermolecular hydrogen bond to TBMP, are slightly elongated at  $1.476(2)$  Å (N1—C1),  $1.469(2)$  Å (N1—C3) and  $1.468(2)$  Å (N1—C5) compared to the mean value of  $1.458$  Å reported for the free aminal cage structure (Rivera *et al.*, 2014) and compared to the C—N2 bond lengths here [ $1.452(2)$  Å (N2—C1),  $1.456(2)$  Å (N2—C2), and  $1.462(2)$  Å (N2—C4)]. This indicates that the formation of the intermolecular hydrogen bonds in the title compound affects the distribution of electron density around this hydrogen-bonded nitrogen centre, resulting in an impact on the respective  $CH_2-N$  single bonds in the heterocyclic cage system.

## 3. Supramolecular features

The most prominent supramolecular feature in this crystal structure is the formation of the expected three-molecule aggregate sustained by two hydroxy-O—H···N hydrogen bonds (Fig. 2). In the crystal packing, roughly in the  $a$ -axis direction, adjacent aggregates are linked by C—H··· $\pi$  interactions with a C—H···Cg distance of  $3.851(2)$  Å and a C—H···Cg angle of  $163^\circ$ , (Table 1). The C—H··· $\pi$  interaction is facilitated between one methylene group (C1—H1*A*) and a symmetry-derived ring (C11—C16; symmetry code:  $-x + 1, -y + 1, -z + 1$ ). These non-covalent interactions lead to the formation of a crystal packing pattern in which the phenol molecules are arranged in an alternating fashion, as is evident when viewed along the [101] direction (Fig. 3).

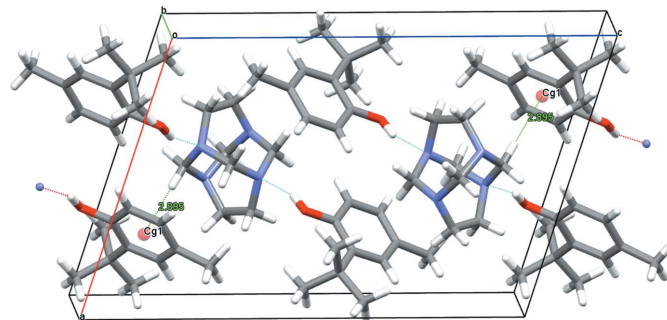
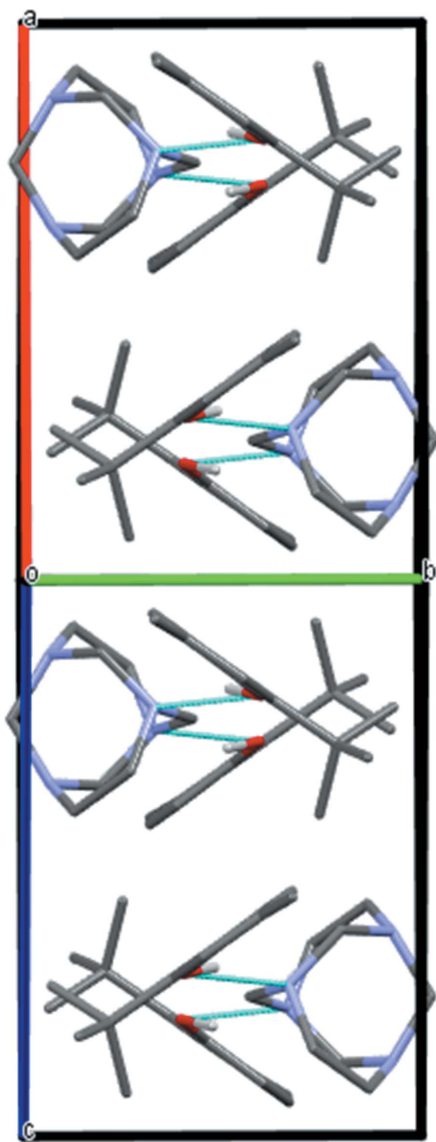


Figure 2

The crystal packing of the title compound viewed roughly along the  $b$ -axis direction, showing the intermolecular O—H···N hydrogen bonds and selected C—H··· $\pi$  interactions.



**Figure 3**  
A partial packing diagram viewed along [101] direction. Dashed lines indicate the intermolecular O—H...N hydrogen bonds. Only H atoms involved in the hydrogen bonds are shown for clarity.

#### 4. Database survey

Using the Cambridge Structural Database (CSD, Version 5.42, September 2021 update; Groom *et al.*, 2016), a search for the title compound structure and names used in this article was conducted with *CONQUEST* (version 2021.2.0; Bruno *et al.*, 2002). The crystal structures of both 2-*tert*-butyl-4-methylphenol (TBMP; Beckmann *et al.*, 2004) and 1,3,6,8-tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane (TATD; Rivera *et al.*, 2014) are already known (refcodes: PAGMEQ and TAZTCD). 2-*tert*-Butyl-4-methylphenol crystallizes with two molecules in the asymmetric unit, which exhibit non-classical intramolecular C—H...O hydrogen bonds similar to what is found in the adduct structure reported here, plus weak intermolecular O—H... $\pi$  interactions. Tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane crystallizes with one quarter of a molecule in the asymmetric unit.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	C <sub>8</sub> H <sub>16</sub> N <sub>4</sub> ·2C <sub>11</sub> H <sub>16</sub> O
<i>M<sub>r</sub></i>	496.72
Crystal system, space group	Monoclinic, <i>P2/c</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.4741 (10), 7.6770 (5), 17.2226 (14)
$\beta$ (°)	108.166 (6)
<i>V</i> (Å <sup>3</sup> )	1441.5 (2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.07
Crystal size (mm)	0.28 × 0.27 × 0.11
Data collection	
Diffractometer	Stoe IPDS II two-circle
Absorption correction	Multi-scan ( <i>X-AREA</i> ; Stoe & Cie, 2001)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.554, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	17127, 3307, 2862
<i>R<sub>int</sub></i>	0.029
( $\sin \theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.653
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.050, 0.132, 1.05
No. of reflections	3307
No. of parameters	170
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.26, -0.19

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

There are no significant differences in the metrical parameters between the structure of the title co-crystal and the singly crystallized entities except for the C—N distances discussed above (section 2).

Co-crystals of tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane have already been reported, *i.e.* with 3-nitrophenol (Rivera *et al.*, 2019), 4-iodophenol (Rivera *et al.*, 2017a), 4-chloro-3,5-dimethylphenol (Rivera *et al.*, 2015a), hydroquinone (Rivera *et al.*, 2007), and 4-bromophenol (Rivera *et al.*, 2015b) (refcodes: HOXGUZ, JELVII, QUFROA, WEXQIA, XULKOG).

In addition, one crystal structure with a singly protonated tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane was determined previously, namely 3,6,8-triaza-1-azoniatricyclo[4.4.1.1<sup>3,8</sup>]dodecane 4-nitrophenolate 4-nitrophenol (Rivera *et al.*, 2017b; refcode: REYKAK).

In another closely related adduct structure, a slightly less sterically crowded alcohol was used bearing an *iso*-propyl instead of the *tert*-butyl substituent on the aromatic ring: tris-[5-methyl-2-(propan-2-yl)phenol]1,3,5,7-tetraazatricyclo[3.3.1.1<sup>3,7</sup>]decane (Mazzeo *et al.*, 2019; refcode: WUTDUN).

#### 5. Synthesis and crystallization

A mixture of 1,3,6,8-tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane (TATD) (1 mmol) and 2-*tert*-butyl-4-methylphenol (TBMP) (2 mmol) was ground using a mortar and pestle at room temperature for 15 min. Completion of the reaction was

monitored by TLC. The mixture was recrystallized from *n*-hexane:chloroform (8:2) solution to obtain colourless crystals suitable for X-ray analysis, m.p. = 374–375 K. (yield: 85%).

## 6. Refinement

The structure of the title compound had been previously deposited by us and was thereby reported as a Private Communication (Bolte *et al.*, 2021, refcode EWICAR). Crystal data, data collection and structure refinement details are summarized in Table 2. The oxygen-bound hydrogen atom was found and refined isotropically without restraints or constraints. Other hydrogen atoms were generated geometrically, and refined with a riding model with C–H = 0.98 Å,  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl, C–H = 0.99 Å,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for methylene, and C–H = 0.95 Å,  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic hydrogen atoms.

## Funding information

Funding for this research was provided by: Facultad de Ciencias, Universidad Nacional de Colombia (grant No. 53864).

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## supporting information

*Acta Cryst.* (2022). E78, 599-602 [https://doi.org/10.1107/S2056989022004972]

## First hydrogen-bonded adduct of sterically hindered 2-*tert*-butyl-4-methylphenol (TBMP) with 1,3,6,8-tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane (TATD) via coupling of classical hydrogen bonds and C—H $\cdots$ $\pi$ non-covalent interactions

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

### 2-*tert*-Butyl-4-methylphenol–\ 1,3,6,8-tetraazatricyclo[4.4.1.1<sup>3,8</sup>]dodecane (2/1)

#### Crystal data

C<sub>8</sub>H<sub>16</sub>N<sub>4</sub>·2C<sub>11</sub>H<sub>16</sub>O  
*M<sub>r</sub>* = 496.72  
 Monoclinic, *P2/c*  
*a* = 11.4741 (10) Å  
*b* = 7.6770 (5) Å  
*c* = 17.2226 (14) Å  
 $\beta$  = 108.166 (6)°  
*V* = 1441.5 (2) Å<sup>3</sup>  
*Z* = 2

*F*(000) = 544  
*D<sub>x</sub>* = 1.144 Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 17127 reflections  
 $\theta$  = 3.6–27.8°  
 $\mu$  = 0.07 mm<sup>-1</sup>  
*T* = 173 K  
 Plate, colourless  
 0.28 × 0.27 × 0.11 mm

#### Data collection

STOE IPDS II two-circle-diffractometer  
 Radiation source: Genix 3D I $\mu$ S microfocus X-ray source  
 $\omega$  scans  
 Absorption correction: multi-scan (X-Area; Stoe & Cie, 2001)  
*T<sub>min</sub>* = 0.554, *T<sub>max</sub>* = 1.000

17127 measured reflections  
 3307 independent reflections  
 2862 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.029  
 $\theta_{\max}$  = 27.6°,  $\theta_{\min}$  = 3.6°  
*h* = -14→14  
*k* = -9→9  
*l* = -22→22

#### Refinement

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.050  
*wR*(*F*<sup>2</sup>) = 0.132  
*S* = 1.05  
 3307 reflections  
 170 parameters  
 0 restraints

Primary atom site location: structure-invariant direct methods  
 Hydrogen site location: mixed  
 H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.4499P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$



$$\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL-2016/6  
(Sheldrick 2015),  
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$   
Extinction coefficient: 0.021 (5)

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.55515 (9)	0.67062 (14)	0.32614 (6)	0.0269 (2)	
N2	0.41669 (11)	0.93222 (15)	0.28288 (7)	0.0334 (3)	
C1	0.47468 (13)	0.80357 (18)	0.34461 (8)	0.0332 (3)	
H1A	0.408781	0.741591	0.359229	0.040*	
H1B	0.523629	0.867230	0.394010	0.040*	
C2	0.30542 (14)	0.8720 (2)	0.22156 (10)	0.0469 (4)	
H2A	0.265533	0.973760	0.188590	0.056*	
H2B	0.248788	0.828122	0.250249	0.056*	
C3	0.31959 (13)	0.7318 (2)	0.16366 (9)	0.0397 (3)	
H3A	0.269762	0.630216	0.169446	0.048*	
H3B	0.284425	0.775888	0.107144	0.048*	
C4	0.500000	1.0300 (3)	0.250000	0.0418 (5)	
H4A	0.449637	1.106627	0.206038	0.050*	0.5
H4B	0.550362	1.106630	0.293961	0.050*	0.5
C5	0.500000	0.5738 (2)	0.250000	0.0282 (4)	
H5A	0.435761	0.497108	0.258605	0.034*	0.5
H5B	0.564238	0.497107	0.241395	0.034*	0.5
O1	0.65236 (10)	0.40303 (14)	0.44346 (6)	0.0399 (3)	
H1	0.6079 (18)	0.482 (3)	0.4109 (12)	0.053 (5)*	
C11	0.69530 (12)	0.46490 (16)	0.52226 (7)	0.0284 (3)	
C12	0.79366 (11)	0.37879 (15)	0.57928 (7)	0.0247 (3)	
C13	0.83508 (11)	0.45122 (17)	0.65783 (7)	0.0280 (3)	
H13	0.901687	0.396088	0.697378	0.034*	
C14	0.78431 (12)	0.59956 (17)	0.68142 (8)	0.0303 (3)	
C15	0.68468 (14)	0.67652 (18)	0.62418 (8)	0.0343 (3)	
H15	0.646455	0.775572	0.638772	0.041*	
C16	0.64080 (14)	0.60914 (18)	0.54571 (8)	0.0350 (3)	
H16	0.572159	0.662490	0.507184	0.042*	
C17	0.85309 (13)	0.21469 (17)	0.55726 (7)	0.0313 (3)	
C18	0.75571 (18)	0.0728 (2)	0.52590 (12)	0.0545 (5)	
H18A	0.717684	0.045775	0.568135	0.082*	
H18B	0.692811	0.114293	0.476635	0.082*	
H18C	0.794385	-0.032304	0.512895	0.082*	
C19	0.95174 (18)	0.1387 (3)	0.63136 (9)	0.0546 (5)	
H19A	0.915053	0.109330	0.674008	0.082*	

H19B	0.986240	0.033393	0.614917	0.082*
H19C	1.017007	0.224808	0.652530	0.082*
C20	0.91373 (19)	0.2589 (3)	0.49204 (11)	0.0565 (5)
H20A	0.852293	0.307854	0.443928	0.085*
H20B	0.979226	0.344302	0.514043	0.085*
H20C	0.948459	0.152887	0.476430	0.085*
C21	0.83767 (16)	0.6747 (2)	0.76656 (9)	0.0441 (4)
H21A	0.895241	0.591026	0.801301	0.066*
H21B	0.771345	0.698204	0.789736	0.066*
H21C	0.880912	0.783389	0.763689	0.066*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0282 (5)	0.0284 (5)	0.0214 (5)	0.0016 (4)	0.0039 (4)	-0.0010 (4)
N2	0.0362 (6)	0.0291 (6)	0.0360 (6)	0.0066 (5)	0.0126 (5)	0.0002 (5)
C1	0.0423 (7)	0.0327 (7)	0.0270 (6)	0.0051 (6)	0.0141 (5)	-0.0016 (5)
C2	0.0303 (7)	0.0566 (10)	0.0495 (9)	0.0131 (7)	0.0064 (6)	-0.0033 (7)
C3	0.0268 (6)	0.0447 (8)	0.0407 (8)	0.0011 (6)	0.0006 (5)	-0.0006 (6)
C4	0.0581 (13)	0.0249 (9)	0.0478 (12)	0.000	0.0242 (10)	0.000
C5	0.0356 (9)	0.0236 (8)	0.0228 (8)	0.000	0.0055 (7)	0.000
O1	0.0527 (6)	0.0388 (6)	0.0200 (4)	0.0145 (5)	-0.0005 (4)	-0.0011 (4)
C11	0.0373 (7)	0.0269 (6)	0.0199 (5)	0.0007 (5)	0.0072 (5)	0.0004 (4)
C12	0.0299 (6)	0.0228 (6)	0.0215 (5)	-0.0008 (5)	0.0082 (4)	-0.0006 (4)
C13	0.0303 (6)	0.0296 (6)	0.0223 (6)	0.0006 (5)	0.0058 (5)	-0.0017 (5)
C14	0.0390 (7)	0.0282 (6)	0.0257 (6)	-0.0038 (5)	0.0128 (5)	-0.0048 (5)
C15	0.0496 (8)	0.0253 (6)	0.0321 (6)	0.0065 (6)	0.0189 (6)	0.0008 (5)
C16	0.0436 (7)	0.0323 (7)	0.0275 (6)	0.0111 (6)	0.0089 (5)	0.0055 (5)
C17	0.0414 (7)	0.0293 (6)	0.0218 (6)	0.0094 (5)	0.0077 (5)	-0.0015 (5)
C18	0.0691 (11)	0.0254 (7)	0.0611 (10)	0.0007 (7)	0.0090 (9)	-0.0098 (7)
C19	0.0657 (11)	0.0584 (10)	0.0316 (7)	0.0367 (9)	0.0033 (7)	-0.0055 (7)
C20	0.0749 (12)	0.0587 (11)	0.0495 (9)	0.0235 (9)	0.0391 (9)	0.0062 (8)
C21	0.0546 (9)	0.0442 (8)	0.0326 (7)	-0.0016 (7)	0.0122 (6)	-0.0157 (6)

*Geometric parameters (Å, °)*

N1—C5	1.4680 (13)	C13—C14	1.3961 (18)
N1—C3 <sup>i</sup>	1.4694 (17)	C13—H13	0.9500
N1—C1	1.4761 (17)	C14—C15	1.3874 (19)
N2—C1	1.4517 (17)	C14—C21	1.5159 (18)
N2—C2	1.456 (2)	C15—C16	1.3868 (19)
N2—C4	1.4615 (16)	C15—H15	0.9500
C1—H1A	0.9900	C16—H16	0.9500
C1—H1B	0.9900	C17—C20	1.533 (2)
C2—C3	1.510 (2)	C17—C19	1.5328 (19)
C2—H2A	0.9900	C17—C18	1.533 (2)
C2—H2B	0.9900	C18—H18A	0.9800
C3—H3A	0.9900	C18—H18B	0.9800

C3—H3B	0.9900	C18—H18C	0.9800
C4—H4A	0.9900	C19—H19A	0.9800
C4—H4B	0.9900	C19—H19B	0.9800
C5—H5A	0.9900	C19—H19C	0.9800
C5—H5B	0.9900	C20—H20A	0.9800
O1—C11	1.3760 (15)	C20—H20B	0.9800
O1—H1	0.88 (2)	C20—H20C	0.9800
C11—C16	1.3920 (18)	C21—H21A	0.9800
C11—C12	1.4086 (17)	C21—H21B	0.9800
C12—C13	1.4016 (16)	C21—H21C	0.9800
C12—C17	1.5353 (17)		
C5—N1—C3 <sup>i</sup>	113.69 (9)	C14—C13—C12	123.91 (12)
C5—N1—C1	114.72 (9)	C14—C13—H13	118.0
C3 <sup>i</sup> —N1—C1	114.05 (11)	C12—C13—H13	118.0
C1—N2—C2	114.42 (12)	C15—C14—C13	117.82 (11)
C1—N2—C4	115.31 (10)	C15—C14—C21	121.34 (12)
C2—N2—C4	114.44 (11)	C13—C14—C21	120.83 (12)
N2—C1—N1	119.16 (10)	C16—C15—C14	120.13 (12)
N2—C1—H1A	107.5	C16—C15—H15	119.9
N1—C1—H1A	107.5	C14—C15—H15	119.9
N2—C1—H1B	107.5	C15—C16—C11	121.33 (12)
N1—C1—H1B	107.5	C15—C16—H16	119.3
H1A—C1—H1B	107.0	C11—C16—H16	119.3
N2—C2—C3	117.06 (12)	C20—C17—C19	107.96 (14)
N2—C2—H2A	108.0	C20—C17—C18	110.29 (14)
C3—C2—H2A	108.0	C19—C17—C18	106.91 (14)
N2—C2—H2B	108.0	C20—C17—C12	109.72 (12)
C3—C2—H2B	108.0	C19—C17—C12	112.10 (10)
H2A—C2—H2B	107.3	C18—C17—C12	109.81 (12)
N1 <sup>i</sup> —C3—C2	116.84 (11)	C17—C18—H18A	109.5
N1 <sup>i</sup> —C3—H3A	108.1	C17—C18—H18B	109.5
C2—C3—H3A	108.1	H18A—C18—H18B	109.5
N1 <sup>i</sup> —C3—H3B	108.1	C17—C18—H18C	109.5
C2—C3—H3B	108.1	H18A—C18—H18C	109.5
H3A—C3—H3B	107.3	H18B—C18—H18C	109.5
N2 <sup>i</sup> —C4—N2	118.16 (16)	C17—C19—H19A	109.5
N2 <sup>i</sup> —C4—H4A	107.8	C17—C19—H19B	109.5
N2—C4—H4A	107.8	H19A—C19—H19B	109.5
N2 <sup>i</sup> —C4—H4B	107.8	C17—C19—H19C	109.5
N2—C4—H4B	107.8	H19A—C19—H19C	109.5
H4A—C4—H4B	107.1	H19B—C19—H19C	109.5
N1—C5—N1 <sup>i</sup>	119.17 (14)	C17—C20—H20A	109.5
N1—C5—H5A	107.5	C17—C20—H20B	109.5
N1 <sup>i</sup> —C5—H5A	107.5	H20A—C20—H20B	109.5
N1—C5—H5B	107.5	C17—C20—H20C	109.5
N1 <sup>i</sup> —C5—H5B	107.5	H20A—C20—H20C	109.5
H5A—C5—H5B	107.0	H20B—C20—H20C	109.5



C11—O1—H1	110.4 (13)	C14—C21—H21A	109.5
O1—C11—C16	120.38 (11)	C14—C21—H21B	109.5
O1—C11—C12	119.23 (11)	H21A—C21—H21B	109.5
C16—C11—C12	120.39 (11)	C14—C21—H21C	109.5
C13—C12—C11	116.33 (11)	H21A—C21—H21C	109.5
C13—C12—C17	121.39 (11)	H21B—C21—H21C	109.5
C11—C12—C17	122.27 (10)		
C2—N2—C1—N1	81.95 (16)	C11—C12—C13—C14	0.39 (19)
C4—N2—C1—N1	-53.89 (17)	C17—C12—C13—C14	-179.70 (12)
C5—N1—C1—N2	-52.30 (16)	C12—C13—C14—C15	1.9 (2)
C3 <sup>i</sup> —N1—C1—N2	81.31 (15)	C12—C13—C14—C21	-177.37 (13)
C1—N2—C2—C3	-67.63 (18)	C13—C14—C15—C16	-1.9 (2)
C4—N2—C2—C3	68.60 (19)	C21—C14—C15—C16	177.41 (14)
N2—C2—C3—N1 <sup>i</sup>	-0.8 (2)	C14—C15—C16—C11	-0.4 (2)
C1—N2—C4—N2 <sup>i</sup>	53.56 (9)	O1—C11—C16—C15	-178.23 (13)
C2—N2—C4—N2 <sup>i</sup>	-82.27 (10)	C12—C11—C16—C15	2.9 (2)
C3 <sup>i</sup> —N1—C5—N1 <sup>i</sup>	-81.55 (10)	C13—C12—C17—C20	-115.74 (15)
C1—N1—C5—N1 <sup>i</sup>	52.24 (8)	C11—C12—C17—C20	64.16 (17)
O1—C11—C12—C13	178.33 (11)	C13—C12—C17—C19	4.20 (19)
C16—C11—C12—C13	-2.75 (19)	C11—C12—C17—C19	-175.90 (14)
O1—C11—C12—C17	-1.58 (19)	C13—C12—C17—C18	122.88 (14)
C16—C11—C12—C17	177.35 (12)	C11—C12—C17—C18	-57.22 (17)

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

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

Cg1 is the centroid of the C11—C16 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 $\cdots$ N1	0.88 (2)	2.01 (2)	2.8534 (15)	161.6 (17)
C18—H18B $\cdots$ O1	0.98	2.30	2.966 (2)	124
C20—H20A $\cdots$ O1	0.98	2.41	3.058 (3)	124
C1—H1A $\cdots$ Cg1 <sup>ii</sup>	0.98	2.90	3.851 (2)	163

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