First hydrogen-bonded adduct of sterically hindered 2-tert-butyl-4-methylphenol (TBMP) with 1,3,6,8-tetraazatricyclo[4.4.1.13,8]dodecane (TATD) via coupling of classical hydrogen bonds and C—H⋯π non-covalent interactions

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The title compound, C₈H₁₆N₄·2C₁₁H₁₆O, 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 P2₁/c with one half of a 1,3,6,8-tetraazatricyclo[4.4.1.1₃,₈]dodecane (TATD) molecule and one 2-tert-butyl-4-methylphenol molecule per asymmetric unit. The crystal structure features intermolecular O—H⋯N hydrogen bonds, as well as intermolecular C—H⋯π 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, 2015a,b, 2017a,b). 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[4.4.1.1₃,₈]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.
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 P21/c. The asymmetric unit comprises one half of a 1,3,6,8-tetraazatricyclo[4.4.1.13,8]dodecane (TATD) molecule and one 2-tert-butyl-4-methylphenol (TBMP) molecule held together by one intermolecular O—H···N hydrogen bond [O···N = 2.8534 (15) Å; O—H···N = 161.6 (17)°; Table 1]. The complete adduct is generated by symmetry by a crystallographic twofold rotation axis, resulting in C2 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—H18B and C20—H20A; 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°. This angle differs from the corresponding more acute torsion angles in free 2-tert-butyl-4-methylphenol (0.73 and −0.56°; 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).

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 CH2—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···π interactions with a C—H···π distance of 3.851 (2) Å and a C—H···π angle of 163°, (Table 1). The C—H···π interaction is facilitated between one methylene group (C11—H1A) 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).

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

| D—H···A    | D—H     | H···A    | D···A    | D—H···A  |
|------------|----------|----------|----------|----------|
| O1—H1···N1 | 0.88 (2)  | 2.01 (2)  | 2.8534 (15) | 161.6 (17) |
| C18—H18B···O1 | 0.98 | 2.41 | 3.058 (3) | 124 |
| C20—H20A···O1 | 0.98 | 2.41 | 3.058 (3) | 124 |
| C1—H1A···Cg1 | 0.98 | 2.90 | 3.851 (2) | 163 |

Symmetry code: (i) −x + 1, −y + 1, −z + 1.
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-tetraaza-tricyclo[4.4.1.13,8]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···N interactions. Tetraaza-tricyclo[4.4.1.13,8]dodecane crystallizes with one quarter of a molecule in the asymmetric unit.

5. Synthesis and crystallization

A mixture of 1,3,6,8-tetraazatriocyclo[4.4.1.13,8]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

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**Table 2**

| Crystal data | Chemical formula | C₁₈H₂₈N₄·2C₁₁H₁₆O |
|---|---|---|
| | M<sub>r</sub> | 496.72 |
| | Crystal system, space group | Monoclinic, P2/c |
| | Temperature (K) | 173 |
| | a, b, c (Å) | 11.4741 (10), 7.6770 (5), 17.2226 (14) |
| | β (°) | 108.166 (6) |
| | V (Å³) | 1441.5 (2) |
| | Z | 2 |
| | Radiation type | Mo Kα |
| | μ (mm⁻¹) | 0.07 |
| | Crystal size (mm) | 0.28 × 0.27 × 0.11 |

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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 tetraazatriocyclo[4.4.1.13,8]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, JEL VII, QUFROA, WEXQIA, XULKOG).

In addition, one crystal structure with a singly protonated tetraazatriocyclo[4.4.1.13,8]dodecane was determined previously, namely 3,6,8-triaza-1-azoniatricyclo[4.4.1.13,7]decane 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-tetraazatriocyclo[3.3.1.13,7]decane (Mazzeo et al., 2019; refcode: WUTDUN).

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**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.
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, \( U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C) \) for methyl, C—H = 0.99 Å, \( U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C) \) for methylene, and C—H = 0.95 Å, \( U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C) \) 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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First hydrogen-bonded adduct of sterically hindered 2-tert-butyl-4-methylphenol (TBMP) with 1,3,6,8-tetraazatricyclo[4.4.1.13,8]dodecane (TATD) via coupling of classical hydrogen bonds and C—H···π 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[4.4.1.13,8]dodecane (2/1)

Crystal data
C₉H₁₆N₄·2C₁₁H₁₆O

| Parameter | Value |
|-----------|-------|
| M_r | 496.72 |
| Monoclinic, P2/c | |
| a | 11.4741 (10) Å |
| b | 7.6770 (5) Å |
| c | 17.2226 (14) Å |
| β | 108.166 (6)° |
| V | 1441.5 (2) Å³ |
| Z | 2 |

Data collection
STOE IPDS II two-circle-diffractometer
Radiation source: Genix 3D μS microfocus X-ray source
ω scans
Absorption correction: multi-scan
(X-Area; Stoe & Cie, 2001)

| Parameter | Value |
|-----------|-------|
| T_min | 0.554 |
| T_max | 1.000 |

Refinement
Refinement on F²
Least-squares matrix: full

| Parameter | Value |
|-----------|-------|
| R[F² > 2σ(F²)] | 0.050 |
| wR(F²) | 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/[σ(F²)² + (0.0663P)² + 0.4499P]
where P = (F² + 2F_C)/3

(Δ/σ) max < 0.001

Acta Cryst. (2022). E78, 599-602
$\Delta \rho_{\text{max}} = 0.26 \text{ e } \AA^{-3}$
$\Delta \rho_{\text{min}} = -0.19 \text{ e } \AA^{-3}$

Extinction correction: SHELXL-2016/6
(Sheldrick 2015),
$Fc^2=kFc[1+0.001xFc^2/\lambda^2]^{-1/4}$
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 ($\AA^2$)

| x     | y     | z     | $U_{eq}$ ($\AA^2$) | 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 | 1.0500 (3) | 0.250000 | 0.0418 (5) |
| H4A   | 0.449637 | 1.106627 | 0.206038 | 0.050* |
| H4B   | 0.550362 | 1.106630 | 0.293961 | 0.050* |
| C5    | 0.500000 | 0.5738 (2) | 0.250000 | 0.0282 (4) |
| H5A   | 0.435761 | 0.497108 | 0.258605 | 0.034* |
| H5B   | 0.564238 | 0.497107 | 0.241395 | 0.034* |
| 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 (Å²)**

|       | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|-------|-------|-------|-------|-------|-------|-------|
| 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—C3i | 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 |        |
| Bond          | Length (Å) | Bond          | Length (Å) |
|--------------|------------|--------------|------------|
| 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     |
| C5—H5B       | 1.3760 (15)| C20—H20B     | 0.9800     |
| O1—C11       | 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)|              |            |

| Bond          | Length (Å) | Bond          | Length (Å) |
|--------------|------------|--------------|------------|
| C5—N1—C3i    | 113.69 (9) | C14—C13—C12 | 123.91 (12)|
| C5—N1—C1     | 114.72 (9) | C14—C13—H13 | 118.0      |
| C3i—N1—C3i   | 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    | 108.9      | 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)|
| N1i—C3—C2    | 116.84 (11)| C17—C18—H18A| 109.5      |
| N1i—C3—H3A   | 108.1      | C17—C18—H18B| 109.5      |
| C2—C3—H3A    | 108.1      | H18A—C18—H18B| 109.5     |
| N1i—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     |
| N2i—C4—N2    | 118.16 (16)| C17—C19—H19A| 109.5      |
| N2i—C4—H4A   | 107.8      | C17—C19—H19B| 109.5      |
| N2—C4—H4A    | 107.8      | H19A—C19—H19B| 109.5     |
| N2i—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—N1i    | 119.17 (14)| C17—C20—H20A| 109.5      |
| N1—C5—H5A    | 107.5      | C17—C20—H20B| 109.5      |
| N1i—C5—H5A   | 107.5      | H20A—C20—H20B| 109.5     |
| N1—C5—H5B    | 107.5      | C17—C20—H20C| 109.5      |
| N1i—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) C21—C21—H21C 109.5

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—C21 1.9 (2)
C3—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) C13—C14—C15—C16 177.41 (14)
N2—C2—C3—N1i −0.8 (2) C13—C14—C15—C16 −1.9 (2)
C1—N2—C4—N2i 53.56 (9) C14—C15—C16—C11 0.4 (2)
C2—N2—C4—N2i −82.27 (10) C11—C12—C17—C20 64.16 (17)
C3—N1—C5—N1i −81.55 (10) C13—C12—C17—C19 −115.74 (15)
C1—N1—C5—N1i 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) C11—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 (Å, °)
Cg1 is the centroid of the C11–C16 ring.

|          | D—H     | H···A   | D···A  | D—H···A  |
|----------|---------|---------|--------|----------|
| O1—H1···N1 | 0.88 (2) | 2.01 (2) | 2.8534 (15) | 161.6 (17) |
| C18—H18B···O1 | 0.98 | 2.30 | 2.966 (2) | 124 |
| C20—H20A···O1 | 0.98 | 2.41 | 3.058 (3) | 124 |
| C1—H1A···Cg1a | 0.98 | 2.90 | 3.851 (2) | 163 |

Symmetry code: (ii) −x+1, −y+1, −z+1.