Crystal structure and Hirshfeld surface analysis of 7,7-dimethyl-2-phenyl-3,3a,4,6,7,8,9,9a-octahydro-1H-benzo[f]isoindole-1,5(2H)-dione

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The title compound, C_{20}H_{23}NO_{2}, was obtained via the reaction of N-allyl-N-phenylacrylamide with 3-iodocyclohex-2-en-1-one using PdCl_{2}(PPh_{3})_{2} as a catalyst. The compound crystallizes in the monoclinic space group P\(\overline{2}_1/c\). The fused-ring system is not planar and the five- and six-membered rings are trans-fused. The molecular geometry is partially stabilized by an intramolecular C—H⋯O hydrogen bond, forming an S(6) ring motif. In the crystal, molecules are linked by C—H⋯O and C—H⋯C interactions into a three-dimensional network. To further analyse the intermolecular interactions, a Hirshfeld surface analysis was performed. The results indicate that the most important contributions to the overall surface are from H⋯H (65.5%), O⋯H/H⋯O (17.5%) and C⋯H/H⋯C (14.3%) interactions.

1. Chemical context

A cascade reaction is a chemical process that comprises at least two consecutive reactions such that each subsequent reaction occurs only by virtue of the chemical functionality formed in the previous step (Nicolaou et al., 2010; Jash et al., 2019; Knowles et al., 2021). Although cascade reactions have been successfully employed for the synthesis of the core skeleton of many important natural products, the design and performance of cascade reactions remain a challenging aspect of organic chemistry (Zhang et al., 2022; Xie & She, 2021). Meanwhile, alkylation of the α position of enones and their derivatives has have drawn considerable attention (Krafft et al., 2005; Muimhneachaí et al., 2017; Shen & Huang, 2008; Zhang et al., 2010; Jana et al., 2021). McGlacken described a Pd-catalysed coupling procedure for tricyclic oxoisochromene derivatives, which represents an example of the α arylation of activated carbocyclic enone-based substrates (Muimhneacháin et al., 2017). Huang and co-workers have realized a series of reactions including Sonogashira coupling, propargyl-allenyl isomerization, and [4 + 2] cycloaddition combined via α alkylation of carbocyclic enone-based substrates, affording an efficient and stereoselective synthesis of polycyclic skeletons (Shen & Huang, 2008). Given this background, we report herein the synthesis and crystal structure of the title compound.
2. Structural commentary

The title compound crystallizes in the monoclinic crystal system in space group $P2_1/c$. Its molecular structure is shown in Fig. 1. The structure of a racemic compound possesses a disordered enantiomer layout (Jacques et al., 1994) and atoms C8 and C9 are found to be disordered. They were both split into two fragments (C8/C22 and C9/C21) and were refined. This refinement led to a 0.805 (10): 0.195 (10) occupancy ratio over two positions for C8 and C9. The site occupancies of C8, C9 and C21, C22 are 0.805 (10) and 0.195 (10), respectively.

The fused ring system is not planar. The $sp^2$-hybridized character of atoms C12 and C13 is confirmed by the C12–C13 [1.350 (3) Å] bond length, and the C11–C12–C15 [114.9 (2)] and C14–C13–C18 [116.3 (2)] bond angles. There is a strong intramolecular hydrogen bond (C2–H2···O1; Table 1), forming an $S(6)$ ring motif.

3. Supramolecular features

The crystal packing of the title compound (Fig. 2) features intermolecular C–H···O hydrogen bonds and C–H···π interactions. The C–H···O interactions are shown as dashed lines. The presence of C–H···π and C–H···O interactions. The absence of adjacent red and blue triangles on the shape-index map (Fig. 4) suggests that there are no notable π–π interactions (C3–H3···O2; C11–H11···Cg3 or C14–H14A···Cg3 or C11–H11D···Cg3 and C14–H14D···Cg3; symmetry codes are given in Table 1). In the crystal, molecules are stacked together layer by layer. Molecules in same layer are linked by C3–H3···O2 interactions, forming a layer parallel to the ab plane (Fig. 2); Molecules in different layers are linked by C11–H11···Cg3 and C14–H14A···Cg3 or C11–H11D···Cg3 and C14–H14D···Cg3 interactions (Fig. 2). In order to investigate the intermolecular interactions in a visual manner, a Hirshfeld surface analysis was performed using CrystalExplorer (Spackman & Jayatilaka, 2009; Turner et al., 2017). The bright-red spots on the Hirshfeld surface mapped over $d_{norm}$ in the range $-0.2740$ (red) to 1.7368 (blue) a.u.

![Figure 1](image1)

The molecular structure of the title compound, with the atom labelling and displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radii.

![Figure 2](image2)

A packing diagram of the title compound. The C–H···π and C–H···O interactions are shown as dashed lines.

![Figure 3](image3)

The Hirshfeld surface mapped over $d_{norm}$ in the range $-0.2740$ (red) to 1.7368 (blue) a.u.

![Figure 4](image4)

The Hirshfeld surface mapped over shape-index.

### Table 1

Hydrogen-bond geometry (Å, °).

| D···A | D–H | H···A | D···A | D–H | H···A |
|-------|------|------|-------|------|------|
| C2–H2···O1 | 0.93 | 2.24 | 2.864 (3) | 124 |
| C3–H3···O2 | 0.93 | 2.53 | 3.4513 (3) | 170 |
| C11–H11A···Cg3 | 0.97 | 2.73 | 3.688 (3) | 168 |
| C11–H11D···Cg3 | 0.97 | 2.95 | 3.688 (3) | 134 |
| C14–H14A···Cg3 | 0.97 | 2.70 | 3.609 (3) | 156 |
| C14–H14D···Cg3 | 0.97 | 2.90 | 3.609 (3) | 131 |

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

Cg3 is the centroid of the C1–C6 ring.
actions. The fingerprint plots (Fig. 5) are given for all contacts, and those delineated into C·O/O·C (0.4%), O·N/N·O (0.5%), C·C (0.7%), N·H/H·N (1.0%), C·H/H·C (14.3%), H·O/O·H (17.5%) and H·H (65.5%). The most important contributions to the crystal packing are H·H and O·H/H·O contacts.

4. Database survey
A search of the Cambridge Structural Database (Version 2021.1; Groom et al., 2016) for compounds having a 3,3a,4,6,7,8,9,9a-octahydro-1H-benzo[fl]isoindole-1,5(2H)-dione fragment gave two hits, including 2a,8,9b-trimethyl-3,4,6,6a,9a,9b-hexahydro[2]benzofuro[1,7-e]isoindole-2,5,7,9-(2aH,8H)-tetrone (I) (Florke, 2019) and 2-ethyl-12,12-dimethyl-4,6,7,8,9,9a-hexahydro-1H-4,9-[1,2]-epicyclobutabenzo[fl]isoindole-1,3,5(2H,3aH)trione (II) (Ma & Gu, 2006). In these two structures, the fused-ring systems are not planar. Compound I crystallizes in the monoclinic crystal system, space group P2₁. The five- and six-membered rings are cis-fused. The crystal structure is characterized by the presence of C—H···O hydrogen bonds. Compound II crystallizes in the orthorhombic crystal system, space group Pbca. The molecules are linked by C—H···O hydrogen bonds, and the crystal packing also features C—H···π interactions.

5. Synthesis and crystallization
N- Allyl-N-phenylacrylamide (0.30 mmol), 3-iodocyclohex-2-en-1-one (0.36 mmol), PdCl2(PPh3)2 (5 mol%, 0.015 mmol, 10.5 mg), TCAB (3,4,3',4'-tetrachloroazobenzene) (10 mol%, 0.03 mmol, 8.33 mg) and K2CO3 (0.36 mmol, 49.68 mg) were stirred in DMF (5.0 mL) at 403 K in a 20 mL tube under an N2 atmosphere. When the reaction was complete (detected by TLC), the mixture was cooled to room temperature. The reaction was quenched with HCl (5%, 10 mL) and extracted with Et2O (3 × 10 mL). The combined organic layers were dried over anhydrous MgSO4 and then evaporated under vacuum. The residue was purified by column chromatography on silica gel using n-hexane/ethyl acetate (10:1 v/v) as eluent to afford the compound as a white solid. Part of the purified product was redissolved in n-hexane/ethyl acetate and colourless crystals suitable for X-ray diffraction were formed after slow evaporation for several days.

Spectroscopic data: IR (film) 2962, 2920, 2885, 1687, 1662, 1619, 1169, 757 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.64–7.62 (m, 2H), 7.41–7.37 (m, 2H), 7.18–7.15 (m, 1H), 3.96–3.93 (m, 1H), 3.68–3.64 (m, 1H), 2.92–2.90 (m, 1H), 2.64–2.61 (m, 1H), 2.43–2.27 (m, 6H), 2.12–2.09 (m, 2H), 1.10 (s, 3H), 1.03 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 198.8, 173.7, 153.8, 139.6, 130.7, 128.9, 124.4, 119.6, 53.0, 51.4, 45.7, 45.1, 36.6, 33.1, 32.3, 29.4, 27.1, 26.3 ppm.

6. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically with C—H = 0.93–0.98 Å and refined as riding atoms. The constraint Ueq(H) = 1.2Ueq(C) or 1.5Ueq(C methyl) was applied in all case. Atoms C8 and C9 are disordered over two positions (A and B) in a 0.805 (10):0.195 (10) occupancy ratio.

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Table 2
Experimental details.

| Crystal data | Chemical formula | C_{20}H_{23}NO_{2} |
|--------------|------------------|-------------------|
| M r (g/mol)  | 329.39 | |
| Crystal system, space group | Monoclinic, P2_1/c |
| Temperature (K) | 200 |
| a, b, c (Å) | 5.7062 (4), 34.009 (3), 8.5042 (8) |
| β (°) | 98.178 (7) |
| V (Å³) | 1633.5 (2) |
| Z | 4 |
| Radiation type | Mo Kα |
| μ (mm⁻¹) | 0.08 |
| Crystal size (mm) | 0.12 x 0.1 x 0.08 |

| Data collection | Diffractometer | Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, AtlasS2 |
|-----------------|----------------|-------------------------------------------------------------|
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2015) |
| T min, T max | 0.621, 1.000 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 6736, 2874, 2046 |
| R int | 0.035 |
| (sin θ/λ) max (Å⁻¹) | 0.595 |

| Refinement | R[F² > 2σ(F²)], wR(F²), S | 0.056, 0.143, 1.05 |
| No. of reflections | 2874 |
| No. of parameters | 229 |
| H-atom treatment | H-atom parameters constrained |
| Δρ max, Δρ min (e Å⁻³) | 0.33, –0.31 |

Computer programs: CrysAlis PRO (Rigaku OD, 2015), SHELXS (Sheldrick, 2008), SHELXL2017/1 (Sheldrick, 2015) and OLEX2 (Dolomanov et al., 2009).

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Computing details

Data collection: CrysAlis PRO (Rigaku OD, 2015); cell refinement: CrysAlis PRO (Rigaku OD, 2015); data reduction: CrysAlis PRO (Rigaku OD, 2015); program(s) used to solve structure: SHELXS (Sheldrick, 2008); program(s) used to refine structure: SHELXL2017/1 (Sheldrick, 2015); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

7,7-Dimethyl-2-phenyl-3,3a,4,6,7,8,9,9a-octahydro-1H-benzo[f]isoindole-1,5(2H)-dione

Crystal data

C₂₀H₂₃NO₂  
Mr = 309.39  
Monoclinic, P2₁/c  
a = 5.7062 (4) Å  
b = 34.009 (3) Å  
c = 8.5042 (8) Å  
β = 98.178 (7)°  
V = 1633.5 (2) Å³  
Z = 4  

Data collection

Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, AtlasS2 diffractometer  
Radiation source: micro-focus sealed X-ray tube, SuperNova (Mo) X-ray Source  
Mirror monochromator  
Detector resolution: 10.5368 pixels mm⁻¹  
ω scans  
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015)  

Refinement

Refinement on F²  
Least-squares matrix: full  
R[F² > 2σ(F²)] = 0.056  
wR(F²) = 0.143  
S = 1.05  
2874 reflections  
229 parameters  
0 restraints

Primary atom site location: structure-invariant direct methods  
Hydrogen site location: inferred from neighbouring sites  
H-atom parameters constrained  
w = 1/[σ²(Fo²) + (0.0507P)² + 0.6477P]  
where P = (Fo² + 2Fc²)/3  
(Δσ)max < 0.001
\( \Delta \rho_{\text{max}} = 0.33 \text{ e Å}^{-3} \)
\( \Delta \rho_{\text{min}} = -0.31 \text{ e Å}^{-3} \)

**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.

**Refinement.** Refinement of \( F^2 \) against ALL reflections. The weighted R-factor \( wR \) and goodness of fit \( S \) are based on \( F^2 \), conventional R-factors R are based on F, with F set to zero for negative F2. The threshold expression of \( F^2 > 2 \sigma(F^2) \) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on \( F^2 \) are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. The C(8) and C(9) is disordered over two positions, site occupancies were refined. This refinement led to a 0.805 : 0.195 ratio in occupancy over two positions for C(8)and C(9).

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å\(^2\))**

| x     | y     | z     | \( U_{\text{eq}} \) | Occ. (<1) |
|-------|-------|-------|------------------|-----------|
| O1    | 1.0478 (3) | 0.74574 (5) | 0.8516 (3) | 0.0677 (7) |
| O2    | 0.3270 (3) | 0.58244 (5) | 0.4595 (2) | 0.0497 (5) |
| N1    | 0.6935 (3) | 0.75875 (5) | 0.6917 (2) | 0.0319 (5) |
| C1    | 0.6910 (4) | 0.80046 (6) | 0.6875 (3) | 0.0312 (5) |
| C2    | 0.8854 (4) | 0.82281 (7) | 0.7539 (3) | 0.0369 (6) |
| H2    | 1.021910 | 0.810308 | 0.802034 | 0.044* |
| C3    | 0.8762 (4) | 0.86346 (7) | 0.7484 (3) | 0.0414 (6) |
| H3    | 1.006620 | 0.878040 | 0.793348 | 0.05* |
| C4    | 0.6759 (4) | 0.88257 (8) | 0.6770 (3) | 0.0444 (6) |
| H4    | 0.670204 | 0.909893 | 0.674013 | 0.053* |
| C5    | 0.4839 (4) | 0.86066 (7) | 0.6099 (3) | 0.0427 (6) |
| H5    | 0.348529 | 0.873425 | 0.561404 | 0.051* |
| C6    | 0.4895 (4) | 0.81998 (7) | 0.6137 (3) | 0.0377 (6) |
| H6    | 0.359101 | 0.805634 | 0.567117 | 0.045* |
| C7    | 0.5009 (4) | 0.73534 (7) | 0.6012 (3) | 0.0359 (6) |
| H7AA  | 0.506687 | 0.736741 | 0.487905 | 0.043* |
| H7AB  | 0.346778 | 0.744172 | 0.622299 | 0.043* |
| H7BC  | 0.454955 | 0.745403 | 0.494562 | 0.043* |
| H7BD  | 0.363048 | 0.733512 | 0.655672 | 0.043* |
| C8    | 0.5547 (7) | 0.69357 (9) | 0.6649 (5) | 0.0308 (10) |
| H8    | 0.492969 | 0.690922 | 0.766149 | 0.037* |
| C9    | 0.8232 (7) | 0.69415 (9) | 0.6983 (5) | 0.0314 (10) |
| H9    | 0.884344 | 0.692311 | 0.596540 | 0.038* |
| C10   | 0.8715 (4) | 0.73524 (7) | 0.7629 (3) | 0.0436 (6) |
| C11   | 0.9147 (4) | 0.65947 (6) | 0.7982 (3) | 0.0346 (6) |
| H11A  | 0.872712 | 0.662201 | 0.904263 | 0.042* |
| H11B  | 1.085889 | 0.658342 | 0.806781 | 0.042* |
| H11C  | 1.058398 | 0.665781 | 0.754796 | 0.042* |
| H11D  | 0.955968 | 0.655544 | 0.911742 | 0.042* |
| C12   | 0.8083 (4) | 0.62222 (6) | 0.7226 (3) | 0.0314 (5) |
| C13   | 0.6101 (4) | 0.62233 (6) | 0.6149 (3) | 0.0320 (5) |
| C14   | 0.4699 (4) | 0.65896 (6) | 0.5612 (3) | 0.0336 (6) |

*Acta Cryst. (2022), E78, 373-376*
## Atomic displacement parameters (Å²)

|    | U¹¹  | U⁻²²  | U⁻³³  | U¹²  | U¹³  | U²³  |
|----|------|-------|-------|------|------|------|
| O1 | 0.0528 (11) | 0.0479 (12) | 0.0885 (16) | −0.0036 (9) | −0.0382 (11) | −0.0010 (11) |
| O2 | 0.0419 (10) | 0.0464 (11) | 0.0556 (12) | −0.0054 (8) | −0.0106 (9) | −0.0023 (9) |
| N1 | 0.0279 (10) | 0.0344 (11) | 0.0323 (11) | −0.0017 (8) | 0.0003 (8) | −0.0006 (9) |
| C1 | 0.0305 (12) | 0.0376 (13) | 0.0257 (12) | −0.0018 (10) | 0.0050 (9) | −0.0018 (10) |
| C2 | 0.0308 (12) | 0.0440 (15) | 0.0351 (14) | −0.0022 (10) | 0.0022 (10) | 0.0006 (11) |
| C3 | 0.0404 (14) | 0.0455 (15) | 0.0379 (15) | −0.0094 (11) | 0.0039 (11) | −0.0036 (12) |
| C4 | 0.0539 (16) | 0.0395 (14) | 0.0394 (15) | −0.0004 (12) | 0.0056 (12) | −0.0007 (12) |
| C5 | 0.0424 (14) | 0.0428 (15) | 0.0419 (15) | 0.0069 (11) | 0.0020 (12) | 0.0019 (12) |
| C6 | 0.0333 (12) | 0.0429 (14) | 0.0358 (14) | −0.0011 (10) | 0.0012 (10) | −0.0022 (11) |
| C7 | 0.0264 (11) | 0.0390 (14) | 0.0394 (15) | −0.0007 (10) | −0.0051 (10) | −0.0027 (11) |
| C8 | 0.022 (2) | 0.0399 (18) | 0.030 (2) | −0.0030 (13) | 0.0017 (16) | 0.0019 (15) |
| C9 | 0.022 (2) | 0.0405 (18) | 0.031 (2) | 0.0015 (13) | 0.0032 (16) | −0.0008 (14) |
| C10 | 0.0362 (13) | 0.0404 (14) | 0.0488 (17) | −0.0015 (11) | −0.0122 (12) | 0.0034 (12) |
| C11 | 0.0277 (11) | 0.0396 (14) | 0.0348 (14) | 0.0007 (9) | −0.0013 (10) | 0.0007 (11) |
| C12 | 0.0259 (11) | 0.0365 (13) | 0.0327 (13) | 0.0002 (9) | 0.0072 (10) | 0.0003 (10) |
| C13 | 0.0275 (11) | 0.0371 (13) | 0.0318 (13) | 0.0006 (9) | 0.0058 (10) | −0.0008 (10) |
| C14 | 0.0274 (11) | 0.0391 (14) | 0.0327 (14) | −0.0018 (9) | −0.0011 (10) | −0.0007 (11) |
| C15 | 0.0301 (12) | 0.0413 (14) | 0.0426 (15) | 0.0033 (10) | 0.0088 (10) | 0.0016 (12) |
| C16 | 0.0328 (13) | 0.0385 (14) | 0.0507 (17) | 0.0037 (10) | 0.0028 (11) | 0.0028 (12) |
| C17 | 0.0430 (14) | 0.0365 (14) | 0.0545 (18) | 0.0007 (11) | −0.0010 (12) | −0.0057 (13) |
supporting information

Geometric parameters (Å, °)

|   | C18     | 0.0356 (13) | 0.0407 (14) | 0.0340 (14) | −0.0042 (10) | 0.0020 (11) | 0.0029 (11) |
|---|---------|-------------|-------------|-------------|--------------|-------------|-------------|
|   | C19     | 0.0433 (15) | 0.0527 (17) | 0.064 (2)   | 0.0019 (12)  | 0.0058 (13) | 0.0148 (14) |
|   | C20     | 0.0474 (15) | 0.0400 (15) | 0.074 (2)   | 0.0076 (12)  | −0.0004 (14)| −0.0008 (14)|
|   | C21     | 0.025 (8)   | 0.035 (7)   | 0.031 (9)   | 0.009 (5)    | 0.016 (7)   | 0.005 (6)   |
|   | C22     | 0.034 (9)   | 0.028 (7)   | 0.041 (10)  | −0.008 (5)   | 0.027 (7)   | −0.001 (6)  |

O1—C10 1.222 (3) C11—H11C 0.9700
O2—C18 1.228 (3) C11—H11D 0.9700
N1—C1  1.419 (3) C11—C12   1.509 (3)
N1—C7  1.481 (3) C11—C21   1.587 (13)
N1—C10 1.365 (3) C12—C13   1.350 (3)
C1—C2  1.396 (3) C12—C15   1.505 (3)
C1—C6  1.397 (3) C13—C14   1.515 (3)
C2—H2  0.9300 C13—C18    1.472 (3)
C2—C3  1.384 (3) C14—H14A  0.9700
C3—H3  0.9300 C14—H14B   0.9700
C3—C4  1.379 (3) C14—H14C  0.9700
C4—H4  0.9300 C14—H14D   0.9700
C4—C5  1.379 (3) C14—C22   1.588 (14)
C5—H5  0.9300 C15—H15A   0.9700
C5—C6  1.384 (3) C15—H15B  0.9700
C6—H6  0.9300 C15—C16    1.525 (3)
C7—H7AA 0.9700 C16—C17   1.523 (4)
C7—H7AB 0.9700 C16—C19   1.533 (3)
C7—H7BC 0.9700 C16—C20   1.531 (3)
C7—H7BD 0.9700 C17—H17A  0.9700
C7—C8  1.535 (4) C17—H17B  0.9700
C7—C22 1.524 (14) C17—C18  1.502 (3)
C8—H8  0.9800 C19—H19A  0.9600
C8—C9  1.518 (7) C19—H19B  0.9600
C8—C14 1.509 (4) C19—H19C  0.9600
C9—H9  0.9800 C20—H20A  0.9600
C9—C10 1.513 (4) C20—H20B  0.9600
C9—C11 1.503 (4) C20—H20C  0.9600
C10—C21 1.586 (14) C21—H21  0.9800
C11—H11A 0.9700 C21—C22  1.43 (3)
C11—H11B 0.9700 C22—H22  0.9800

C1—N1—C7 121.36 (17) C13—C12—C15 122.8 (2)
C10—N1—C1 126.93 (19) C15—C12—C11 114.87 (19)
C10—N1—C7 111.47 (18) C12—C13—C14 124.2 (2)
C2—C1—N1 122.0 (2)   C12—C13—C18 119.5 (2)
C2—C1—C6  118.6 (2)   C18—C13—C14 116.28 (19)
C6—C1—N1  119.41 (19) C8—C14—C13 110.7 (2)
C1—C2—H2  119.8  C8—C14—H14A 109.5
C3—C2—C1  120.4 (2)   C8—C14—H14B 109.5

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| Bond | Angle (°) | Bond | Angle (°) |
|------|----------|------|----------|
| C3—C2—H2   | 119.8    | C13—C14—H14A | 109.5    |
| C2—C3—H3   | 119.6    | C13—C14—H14B | 109.5    |
| C4—C3—C2   | 120.7 (2) | C13—C14—H14C | 109.9    |
| C4—C3—H3   | 119.6    | C13—C14—H14D | 109.9    |
| C3—C4—H4   | 120.4    | C13—C14—C22  | 108.9 (6) |
| C3—C4—C5   | 119.2 (2) | H14A—C14—H14B | 108.1    |
| C5—C4—H4   | 120.4    | H14C—C14—H14D | 108.3    |
| C4—C5—H5   | 119.5    | C22—C14—H14C | 109.9    |
| C4—C5—C6   | 121.1 (2) | C22—C14—H14D | 109.9    |
| C6—C5—H5   | 119.5    | C12—C15—H15A | 108.3    |
| C1—C6—H6   | 120.0    | C12—C15—H15B | 108.3    |
| C5—C6—C1   | 120.0 (2) | C12—C15—C16  | 116.00 (19) |
| C5—C6—H6   | 120.0    | H15A—C15—H15B | 107.4    |
| N1—C7—H7AA | 111.3    | C16—C15—H15A | 108.3    |
| N1—C7—H7AB | 111.3    | C16—C15—H15B | 108.3    |
| N1—C7—H7BC | 112.2    | C15—C16—C19  | 110.3 (2) |
| N1—C7—H7BD | 112.2    | C15—C16—C20  | 110.48 (19) |
| N1—C7—C8   | 102.57 (19) | C17—C16—C15 | 107.5 (2) |
| N1—C7—C22  | 97.7 (6) | C17—C16—C19 | 110.1 (2) |
| H7BC—C7—H7BD | 109.8 | C20—C16—C19 | 108.5 (2) |
| C8—C7—H7AA | 111.3    | C16—C17—H17A | 109.1    |
| C8—C7—H7AB | 111.3    | C16—C17—H17B | 109.1    |
| C22—C7—H7BC | 112.2  | H17A—C17—H17B | 107.9    |
| C22—C7—H7BD | 112.2  | C18—C17—C16 | 112.4 (2) |
| C7—C8—H8   | 108.4    | C18—C17—H17A | 109.1    |
| C9—C8—C7   | 101.5 (3) | C18—C17—H17B | 109.1    |
| C9—C8—H8   | 108.4    | O2—C18—C13  | 122.0 (2) |
| C14—C8—C7  | 119.0 (3) | O2—C18—C17  | 121.2 (2) |
| C14—C8—H8  | 108.4    | C13—C18—C17  | 116.8 (2) |
| C14—C8—C9  | 110.5 (4) | C16—C19—H19A | 109.5    |
| C8—C9—H9   | 108.1    | C16—C19—H19B | 109.5    |
| C10—C9—C8  | 101.9 (3) | C16—C19—H19C | 109.5    |
| C10—C9—H9  | 108.1    | H19A—C19—H19B | 109.5    |
| C11—C9—C8  | 110.8 (4) | H19A—C19—H19C | 109.5    |
| C11—C9—H9  | 108.1    | H19B—C19—H19C | 109.5    |
| C11—C9—C10 | 119.3 (3) | C16—C20—H20A | 109.5    |
| O1—C10—N1  | 126.8 (2) | C16—C20—H20B | 109.5    |
| O1—C10—C9  | 125.9 (2) | C16—C20—H20C | 109.5    |
| O1—C10—C21 | 127.6 (5) | H20A—C20—H20B | 109.5    |
| N1—C10—C9  | 107.1 (2) | H20A—C20—H20C | 109.5    |
| N1—C10—C21 | 100.0 (5) | H20B—C20—H20C | 109.5    |
| C9—C11—H11A| 109.8    | C10—C21—H21  | 113.3    |
| C9—C11—H11B| 109.8    | C11—C21—C10  | 110.2 (10) |
| C9—C11—C12 | 109.4 (2) | C11—C21—H21  | 113.3    |
| H11A—C11—H11B | 108.2 | C22—C21—C10  | 94.6 (12) |
| H11C—C11—H11D | 108.1 | C22—C21—C11  | 110.6 (14) |
| C12—C11—H11A | 109.8 | C22—C21—H21  | 113.3    |
| Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|--------------|--------------|--------------|
| C12—C11—H11B | 109.8        | C7—C22—C14  | 114.8 (10)   |
| C12—C11—H11C | 109.5        | C7—C22—H22  | 111.1        |
| C12—C11—H11D | 109.5        | C14—C22—H22 | 111.1        |
| C12—C11—C21  | 110.6 (5)    | C21—C22—C7  | 99.4 (13)    |
| C21—C11—H11C | 109.5        | C21—C22—C14 | 108.8 (14)   |
| C21—C11—H11D | 109.5        | C21—C22—H22 | 111.1        |
| C13—C12—C11  | 122.3 (2)    |              |              |

### Suppl. Table 1

| Bond          | Torsion Angle (°) | Bond          | Torsion Angle (°) |
|--------------|------------------|--------------|------------------|
| O1—C10—C21—C11 | -41.8 (15)       | C10—N1—C7—C22 | -13.4 (8)        |
| O1—C10—C22—C21 | -155.8 (9)       | C10—C9—C11—C12 | 169.8 (3)        |
| N1—C1—C2—C3  | -179.6 (2)       | C10—C21—C22—C7 | -58.3 (14)       |
| N1—C1—C6—C5  | 179.5 (2)        | C10—C21—C22—C14 | -178.7 (7)       |
| N1—C7—C8—C9  | -33.0 (4)        | C11—C9—C10—O1 | 32.6 (6)         |
| N1—C7—C8—C14 | -154.5 (3)       | C11—C9—C10—N1 | -153.1 (3)       |
| N1—C7—C22—C14 | 162.6 (11)       | C11—C12—C13—C14 | -1.6 (3)         |
| N1—C7—C22—C21 | 46.7 (14)        | C11—C12—C13—C18 | 176.29 (19)     |
| N1—C10—C21—C11 | 163.7 (8)       | C11—C12—C15—C16 | 167.2 (2)       |
| N1—C10—C21—C22 | 49.7 (14)       | C11—C21—C22—C7 | -171.9 (7)      |
| C1—N1—C7—C8  | -170.1 (3)       | C11—C21—C22—C14 | 67.7 (19)       |
| C1—N1—C7—C22 | 161.4 (8)        | C12—C11—C21—C10 | -151.1 (7)      |
| C1—N1—C10—O1 | 9.5 (4)          | C12—C11—C21—C22 | -47.8 (17)      |
| C1—N1—C10—C9 | -164.7 (3)       | C12—C13—C14—C8 | -10.3 (4)       |
| C1—N1—C10—C21 | 164.3 (7)       | C12—C13—C14—C22 | 19.4 (8)        |
| C1—C2—C3—C4  | -0.3 (3)         | C12—C13—C18—O2 | 168.4 (2)       |
| C2—C1—C6—C5  | -1.2 (3)         | C12—C13—C18—C17 | -13.5 (3)       |
| C2—C3—C4—C5  | -0.3 (4)         | C12—C15—C16—C17 | 42.8 (3)        |
| C3—C4—C5—C6  | 0.2 (4)          | C12—C15—C16—C19 | -77.2 (3)       |
| C4—C5—C6—C1  | 0.6 (3)          | C12—C15—C16—C20 | 162.8 (2)       |
| C6—C1—C2—C3  | 1.0 (3)          | C13—C12—C15—C16 | -14.9 (3)       |
| C7—N1—C1—C2  | -171.0 (2)       | C13—C14—C22—C7 | -162.6 (9)      |
| C7—N1—C1—C6  | 8.4 (3)          | C13—C14—C22—C21 | -52.3 (17)      |
| C7—N1—C10—O1 | -176.1 (3)       | C14—C8—C9—C10 | 165.6 (2)       |
| C7—N1—C10—C9 | 9.7 (3)          | C14—C8—C9—C11 | -66.4 (5)       |
| C7—N1—C10—C21 | -21.3 (7)       | C14—C13—C18—O2 | -13.5 (3)       |
| C7—C8—C9—C10 | 38.4 (5)         | C14—C13—C18—C17 | 164.6 (2)       |
| C7—C8—C9—C11 | 166.4 (2)        | C15—C12—C13—C14 | -179.4 (2)      |
| C7—C8—C14—C13 | 159.4 (3)       | C15—C12—C13—C18 | -1.4 (3)        |
| C8—C9—C10—O1 | 155.0 (3)        | C15—C16—C17—C18 | -56.9 (2)       |
| C8—C9—C10—N1 | -30.7 (4)        | C16—C17—C18—O2 | -137.6 (2)      |
| C8—C9—C11—C12 | 52.0 (5)         | C16—C17—C18—C13 | 44.2 (3)        |
| C9—C8—C14—C13 | 42.5 (5)         | C18—C13—C14—C8 | 171.7 (3)       |
| C9—C11—C12—C13 | -19.3 (4)       | C18—C13—C14—C22 | -158.6 (8)      |
| C9—C11—C12—C15 | 158.6 (3)       | C19—C16—C17—C18 | 63.3 (3)        |
| C10—N1—C1—C2  | 2.9 (3)          | C20—C16—C17—C18 | -177.2 (2)      |
| C10—N1—C1—C6  | -177.7 (2)       | C21—C11—C12—C13 | 13.7 (8)        |
| C10—N1—C7—C8  | 15.1 (3)         | C21—C11—C12—C15 | -168.4 (8)      |
Hydrogen-bond geometry (Å, °)

$Cg3$ is the centroid of the C1–C6 ring.

| $D$—$H$···$A$ | $D$—$H$ | $H$···$A$ | $D$···$A$ | $D$—$H$···$A$ |
|---------------|---------|---------|---------|-------------|
| C2—H2···O1    | 0.93    | 2.24    | 2.864 (3)| 124         |
| C3—H3···O2$^i$| 0.93    | 2.53    | 3.4513 (3)| 170         |
| C11—H11A···$Cg3^{ii}$ | 0.97 | 2.73    | 3.688 (3) | 168         |
| C11—H11D···$Cg3^{ii}$ | 0.97 | 2.95    | 3.688 (3) | 134         |
| C14—H14A···$Cg3^{iii}$ | 0.97 | 2.70    | 3.609 (3) | 156         |
| C14—H14D···$Cg3^{iii}$ | 0.97 | 2.90    | 3.609 (3) | 131         |

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