Crystal structure and Hirshfeld surface analysis of 2-amino-4-(4-methoxyphenyl)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile

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The central tetrahydropyridine ring of the title compound, C_{19}H_{17}N_{3}O_{2}, adopts a screw-boat conformation. In the crystal, strong C—H···O and N—H···N hydrogen bonds form dimers with $R_{2}^{2}(14)$ and $R_{2}^{2}(12)$ ring motifs, respectively, between consecutive molecules along the $c$-axis direction. Intermolecular N—H···O and C—H···O hydrogen bonds connect these dimers, forming a three-dimensional network. C—H···π interactions and π···π stacking interactions contribute to the stabilization of the molecular packing. A Hirshfeld surface analysis indicates that the contributions from the most prevalent interactions are H···H (47.1%), C···H/H···C (20.9%), O···H/H···O (15.3%) and N···H/H···N (11.4%).

1. Chemical context

Carbon–carbon and carbon–nitrogen bond-forming reactions represent an important synthetic class in organic chemistry (Yadigarov et al., 2009; Abdelhamid et al., 2011; Yin et al., 2020; Khalilov et al., 2021). Notably, pyridine derivatives are widely applied in the discovery of biologically active molecules and multifunctional materials (Magerramov et al., 2018; Sherman & Murugan, 2015; Mamedov et al., 2020). On the other hand, the tetrahydropyridine moiety is an essential part of diverse biologically active compounds, food additives and natural products (Mateeva et al., 2005).

In the framework of ongoing structural studies (Safavora et al., 2019; Naghibiyev et al., 2020; 2021a,b; Maharramov et al., 2021), we report here the crystal structure and Hirshfeld surface analysis of the title compound, 2-amino-4-(4-methoxyphenyl)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile.
2. Structural commentary

The title compound (Fig. 1) crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. The central N1/C2–C6 tetrahydropyridine ring of the molecule adopts a screw-boat conformation with puckering parameters (Cremer & Pople, 1975) $Q_T = 0.503 (2)$ Å, $\theta = 66.1 (2)^\circ$, $\phi = 153.3 (2)^\circ$. The C7–C12 phenyl ring, which is attached to N1, is in an equatorial position and makes a dihedral angle of $54.43 (9)^\circ$ with the mean plane of the tetrahydropyridine ring. The C13–C18 methoxyphenyl ring, which is attached to C4, is in an axial position. The dihedral angle between the C7–C12 phenyl and C13–C18 methoxyphenyl rings is $68.61 (10)^\circ$.

3. Supramolecular features

As shown in Fig. 2, strong intermolecular C11–H11⋯O1 and N3–H3⋯N2 hydrogen bonds (Table 1) form dimers with $R_{2}^{2}(14)$ and $R_{2}^{2}(12)$ ring motifs (Bernstein et al., 1995), respectively, between adjacent molecules along the $c$-axis direction. These dimers are connected by N3–H3⋯O2 and C14–H14⋯O1 hydrogen bonds, forming a three-dimensional network (Table 1; Fig. 3). Furthermore, C⋯H stacking interactions ($Cg_3$ is the centroid of the C13–C18 methoxyphenyl ring; Table 1) and C⋯C stacking interactions ($Cg_2$ is the centroid of the C7–C12 phenyl ring) contribute to the stabilization of the molecular packing (Figs. 4 and 5).

4. Hirshfeld surface analysis

The Hirshfeld surface analysis was performed and the associated two dimensional fingerprint plots generated using
Crystal Explorer 17 (Turner et al., 2017). The Hirshfeld surface was calculated using a standard (high) surface resolution with the three-dimensional $d_{norm}$ surface plotted over a fixed colour scale mapped over the range $0.4835$ (red) to $1.8469$ (blue) a.u. The $d_{norm}$ mapping indicates that strong hydrogen-bonding interactions, such as N—H···N, N—H···O and C—H···O hydrogen bonds (Tables 1 and 2), appear to be the primary interactions in the structure, seen as a bright-red area in the Hirshfeld surface (Fig. 6).

The Hirshfeld surface mapped over electrostatic potential (Spackman et al., 2008) is shown in Fig. 7. The blue regions indicate positive electrostatic potential (hydrogen-bond

Figure 4
A general view of the C—H··π interactions and π–π stacking interactions in the crystal packing of the title compound (symmetry codes: (iii) $-x + 1, -y + 1, -z + 1$; (v) $-x + 1, 1/2 + y, 1/2 - z + 1$).

Figure 5
The crystal packing of the title compound, viewed along the $b$ axis, showing the C—H··π interactions and π–π stacking interactions as dashed lines.

Figure 6
Hirshfeld surface mapped over $d_{norm}$ showing the N—H···N, N—H···O and C—H···O intermolecular contacts.

Figure 7
View of the three-dimensional Hirshfeld surface of the title compound, showing the hydrogen-bonding interactions, plotted over electrostatic potential energy in the range $-0.0500$ to $0.0500$ a.u. using the STO-3 G basis set at the Hartree–Fock level of theory. Hydrogen-bond donors and acceptors are shown as blue and red regions, respectively, around the atoms, corresponding to positive and negative potentials.
The percentage contributions of the C···C, C···N/N···C and N···N contacts are negligible, at 3.1, 1.4 and 0.8%, respectively. The predominance of H···H, C···H/H···C, O···H/H···O and N···H/H···N contacts indicate that van der Waals interactions and hydrogen bonding play the major roles in the crystal packing (Hathwar et al., 2015).

5. Database survey
A search of the Cambridge Structural Database (CSD, version 5.42, update of September 2021; Groom et al., 2016) found four compounds with the 6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine unit that are similar to the title compound, viz. 5-acetyl-2-amino-4-(4-bromophenyl)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile (I) (YAXQAT; Mamedov et al., 2022), 2-amino-4-(2,6-dichlorophenyl)-5-(1-hydroxyethylidene)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile (II) (OZAKOS, Naghiyev et al., 2021c), methyl 6-oxo-4-phenyl-2-[{1(Z)-2-((pyridin-2-yl)ethenyl)1,4,5,6-tetrahydropyridine-3-carboxylate (III) (PEDFEL, Smits et al., 2012) and ethyl 5-ethoxymethylene-2-methyl-6-oxo-4-phenyl-1,4,5,6-tetrahydropyridine-3-carboxylate (IV) (VAGXAD, Novoa de Armas et al., 2003).

Compound (I) crystallizes in the monoclinic space group Pc with Z = 4, and with two molecules, A and B, in the asymmetric unit. These molecules are stereoisomers with an R,R absolute configuration at C3 and C4 in molecule A, whereas the corresponding atoms in B, C23 and C24, have an S configuration. In both molecules, the conformation of the central dihydropyridine ring is close to screw-boat. The molecular conformation is stabilized by N—H···O hydrogen bonds, forming a dimer with an R2(6)(16) ring motif. Both molecules of the dimers are connected by intermolecular N—H···O hydrogen bonds with an R2(14) ring motif into chains along the c-axis direction. Furthermore C—Br···π and C==O···π stacking interactions between these ribbons contribute to the stabilization of the molecular packing.

Compound (II) crystallizes in the monoclinic space group P21/c with Z = 4 and the asymmetric unit comprises one molecule. The central tetrahydropyridine ring is almost planar with a maximum deviation of 0.074 (3) Å for C4. The phenyl and dichlorophenyl rings are at an angle of 21.28 (15)°. They form dihedral angles of 86.10 (15) and 87.17 (14)°, respectively, with the central tetrahydropyridine ring. A strong intramolecular O2—H2···O1 hydrogen bond stabilizes the molecular conformation of the molecule, creating an S(6) ring motif. In the crystal, molecules are linked by intermolecular N—H···N and C—H···N hydrogen bonds, and N—H···π and C—H···π interactions, forming a three-dimensional network.

In molecule (III) (monoclinic space group P21/c, Z = 4), the cis configuration of the pyridinyl-vinyl fragment is stabilized by a strong intramolecular N—H···N hydrogen bond. The phenyl and pyridine rings are inclined to one another by 77.3 (1)°. In the crystal, inversion dimers are present via pairs of C—H···O hydrogen bonds and are further linked by C—H···O hydrogen bonds and C—H···π interactions.

Figure 8
(a) The full two-dimensional fingerprint plot for the title compound and those delineated into (b) H···H (47.1%), (c) C···H/H···C (20.9%), (d) O···H/H···O (15.3%) and (e) N···H/H···N (11.4%) contacts.

Table 2
Summary of short interatomic contacts (Å) in the title compound.

| Contact | Distance | Symmetry operation |
|---------|----------|-------------------|
| O1···H14 | 2.48 | x, 1 + y, z |
| H11···O1 | 2.55 | 1 – x, 1 – y, 1 – z |
| N2···H7 | 2.70 | 1 + y, 1/2 + y, 1/2 + z |
| O2···H3D | 2.48 (2) | 1/2 + x, 1/2 – y, 1/2 + z |
| H3C···N2 | 2.10 (3) | -x, y, 1/2 – z |
| C20···C6 | 3.318 (3) | -x, 1 – y, 1 – z |

The two-dimensional fingerprint plots are illustrated in Fig. 8. H···H contacts comprise 47.1% of the total interactions (Fig. 8b), followed by C···H/H···C (Fig. 8c; 20.9%), O···H/H···O (Fig. 8d; 15.3%) and N···H/H···N (Fig. 8e; 11.4%).
6. Synthesis and crystallization

To a solution of 2-(4-methoxybenzylidene)malononitrile (0.94 g; 5.1 mmol) and acetoacetonilide (0.92 g; 5.2 mmol) in methanol (25 mL), 3–4 drops of piperidine were added and the mixture was stirred at 328–333 K for 10 min and was kept at room temperature for 48 h. Then 15 mL of methanol were removed from the reaction mixture, which was left overnight. The precipitated crystals were separated by filtration and recrystallized from ethanol/water (1:1) solution (yield 61%; m.p. 471–472 K).

1H NMR (300 MHz, DMSO-d$_6$, ppm.): 2.80 (dd–dd, 1H, CH$_2$); 3.19 (dd–dd, 1H, CH$_2$); 3.82 (s, 3H, OCH$_3$); 3.93 (t, 1H, CH); 5.85 (s, 2H, NH$_2$); 7.15–7.58 (m, 9H, 2Ar–H). $^{13}$C NMR (75 MHz, DMSO-d$_6$, ppm.): 36.06 (CH–Ar), 40.42 (CH$_2$), 53.78 (OCH$_3$), 59.05 (C$_{quat}$), 112.89 (2CH$_{ar}$), 121.21 (CN), 128.61 (1CH$_{ar}$), 128.88 (2CH$_{ar}$), 130.44 (2CH$_{ar}$), 130.51 (2CH$_{ar}$), 136.06 (C$_{ar}$, quat.), 137.02 (C$_{ar}$, quat.), 154.59 (C$_{ar}$, quat.), 155.18 (C$_{quat}$), 168.82 (N–C=O).

7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms bonded to nitrogen were located in a difference-Fourier map, and only their positional parameters were refined [N3–H3C = 0.91 (2) and N3–H3D = 0.91 (2) Å with $U_{iso}(H)$ = 1.2$U_{eq}(N)$]. C-bound H atoms were positioned geometrically, with C–H = 0.95–1.00 Å, and were refined with $U_{iso}(H)$ = 1.2$U_{eq}(C)$ or 1.5$U_{eq}(C)-methyl$.

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Authors’ contributions are as follows. Conceptualization, KAA and EZH; methodology, EZH and KAA; investigation, KAA, MA and EVD; writing (original draft), MA and KAA; writing (review and editing of the manuscript), MA and EZH; visualization, MA, EZH and KAA; funding acquisition, VNK, ATH and AAA; resources, AAA, VNK and KAA; supervision, KAA and MA.

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### Table 3: Experimental details.

| Crystal data | C$_{13}$H$_{17}$N$_3$O$_2$ | $M_r$ | 319.36 |
|--------------|-------------------------|------|-------|
| Chemical formula | Monoclinic, $P2_1/n$ | Temperature (K) | 100 |
| Crystal system, space group | | $a$, $b$, $c$ (Å) | 12.910 (3), 6.3200 (13), 21.170 (4) |
| | | $\beta$ (°) | 106.48 (3) |
| | | $\gamma$ (°) | 1656.3 (7) |
| | | $Z$ | 4 |
| Radiation type | Synchrotron | $\mu$ (mm$^{-1}$) | 0.11 |
| | | Crystal size (mm) | 0.40 × 0.15 × 0.07 |

### Data collection

Diffractometer | Rayonix SX165 CCD |
|---------------|------------------|
| Absorption correction | Multi-scan (SCALA; Evans, 2006) |
| No. of measured, independent and observed $| F^2 > 2\sigma(F^2) $ | 26143, 3603, 3125 |
| $R_{int}$ | 0.049 |
| $\langle \sin \theta/\lambda \rangle_{max}$ (Å$^{-1}$) | 0.643 |

### Refinement

$| R[F^2 > 2\sigma(F^2)] |$, $wR(F^2)$, $S$ | 0.054, 0.143, 1.05 |
| No. of reflections | 3603 |
| No. of parameters | 225 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |

$\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å$^{-3}$) | 0.29, −0.27 |
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Crystal structure and Hirshfeld surface analysis of 2-amino-4-(4-methoxy-phenyl)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile

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Computing details
Data collection: Marcdd (Doyle, 2011); cell refinement: iMosflm (Battye et al., 2011); data reduction: iMosflm (Battye et al., 2011); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: PLATON (Spek, 2020).

2-Amino-4-(4-methoxyphenyl)-6-oxo-1-phenyl-1,4,5,6-tetrahydropyridine-3-carbonitrile

Crystal data
C₁₉H₁₇N₃O₂
Mr = 319.36
Monoclinic, P2₁/n
a = 12.910 (3) Å
b = 6.3200 (13) Å
c = 21.170 (4) Å
β = 106.48 (3)°
V = 1656.3 (7) Å³
Z = 4
F(000) = 672
Dₐ = 1.281 Mg m⁻³
Synchrotron radiation, λ = 0.80246 Å
Cell parameters from 600 reflections
θ = 2.4–30.0°
µ = 0.11 mm⁻¹
T = 100 K
Prism, colourless
0.40 × 0.15 × 0.07 mm

Data collection
Rayonix SX165 CCD diffractometer
/θ scan
Absorption correction: multi-scan
(Scala;Evans, 2006)
Tmin = 0.950, Tmax = 0.985
26143 measured reflections
3603 independent reflections
3125 reflections with I > 2σ(I)
Rint = 0.049
θmax = 31.1°, θmin = 2.3°
h = −16→16
k = −8→7
l = −27→27

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.054
wR(F²) = 0.143
S = 1.05
3603 reflections
225 parameters
0 restraints
Primary atom site location: difference Fourier map
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(F²) + (0.059P)² + 1.3785P]
where P = (F² + 2F²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.29 e Å^{-3}
Δρ_{min} = −0.27 e Å^{-3}

Extinction correction: SHELXL,
Fc^2 = kFc[1+0.001xFc^2/λ^2/sin(2θ)]^{1/4}
Extinction coefficient: 0.033 (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.

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

| x      | y      | z       | U_{iso} / U_{eq} |
|--------|--------|---------|------------------|
| O1     | 0.33220 (11) | 0.8608 (2) | 0.55256 (7) | 0.0332 (3) |
| O2     | 0.55206 (12) | 0.1472 (3) | 0.79862 (7) | 0.0413 (4) |
| N1     | 0.24126 (11) | 0.5628 (2) | 0.50951 (7) | 0.0269 (3) |
| N2     | -0.03015 (13) | 0.1368 (3) | 0.56257 (8) | 0.0321 (4) |
| N3     | 0.12078 (12) | 0.3027 (3) | 0.45307 (8) | 0.0300 (4) |
| H3C    | 0.0857 (18) | 0.177 (4) | 0.4520 (11) | 0.036* |
| H3D    | 0.1458 (19) | 0.336 (4) | 0.4183 (12) | 0.036* |
| C2     | 0.26361 (14) | 0.7307 (3) | 0.55371 (9) | 0.0272 (4) |
| C3     | 0.19790 (14) | 0.7407 (3) | 0.60221 (9) | 0.0287 (4) |
| H3A    | 0.1284 | 0.8122 | 0.5814 | 0.034* |
| H3B    | 0.2372 | 0.8254 | 0.6409 | 0.034* |
| C4     | 0.17589 (14) | 0.5196 (3) | 0.62495 (9) | 0.0277 (4) |
| C5     | 0.1221 | 0.5339 | 0.6506 | 0.033* |
| C6     | 0.12391 (13) | 0.3942 (3) | 0.56355 (9) | 0.0268 (4) |
| C7     | 0.15916 (13) | 0.4149 (3) | 0.50888 (9) | 0.0262 (4) |
| H8     | 0.2765 | 0.8249 | 0.4215 | 0.041* |
| C9     | 0.38256 (17) | 0.6690 (4) | 0.38261 (11) | 0.0408 (5) |
| H9     | 0.3906 | 0.7800 | 0.3541 | 0.049* |
| C10    | 0.43779 (17) | 0.4806 (4) | 0.38357 (11) | 0.0421 (5) |
| H10    | 0.4827 | 0.4624 | 0.3554 | 0.051* |
| C11    | 0.42768 (16) | 0.3194 (4) | 0.42533 (10) | 0.0379 (5) |
| H11    | 0.4651 | 0.1898 | 0.4256 | 0.045* |
| C12    | 0.36267 (15) | 0.3466 (3) | 0.46698 (9) | 0.0314 (4) |
| H12    | 0.3564 | 0.2370 | 0.4964 | 0.038* |
| C13    | 0.27801 (14) | 0.4188 (3) | 0.66992 (9) | 0.0266 (4) |
| C14    | 0.32417 (14) | 0.2403 (3) | 0.65102 (9) | 0.0274 (4) |
| H14    | 0.2927 | 0.1822 | 0.6085 | 0.033* |
| C15    | 0.41514 (15) | 0.1438 (3) | 0.69241 (9) | 0.0298 (4) |
| H15    | 0.4443 | 0.0197 | 0.6787 | 0.036* |
| C16    | 0.46259 (15) | 0.2306 (3) | 0.75379 (9) | 0.0316 (4) |
| H17    | 0.4520 | 0.4735 | 0.8153 | 0.040* |
| C18    | 0.32761 (15) | 0.5043 (3) | 0.73205 (9) | 0.0301 (4) |
| H18    | 0.2980 | 0.6273 | 0.7460 | 0.036* |
### Atomic displacement parameters (Å²)

|     | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|-----|------------|------------|------------|------------|------------|------------|
| O1  | 0.0328 (7) | 0.0278 (7) | 0.0408 (7) | −0.0063 (5)| 0.0132 (6) | −0.0045 (6)|
| O2  | 0.0378 (7) | 0.0485 (9) | 0.0319 (7) | 0.0068 (6) | 0.0005 (6) | 0.0031 (6) |
| N1  | 0.0262 (7) | 0.0245 (7) | 0.0304 (7) | −0.0025 (6)| 0.0086 (6) | −0.0026 (6)|
| N2  | 0.0318 (8) | 0.0294 (8) | 0.0348 (8) | −0.0028 (6)| 0.0093 (6) | 0.0009 (7) |
| N3  | 0.0311 (8) | 0.0297 (8) | 0.0288 (8) | −0.0072 (6)| 0.0079 (6) | −0.0025 (6)|
| C2  | 0.0272 (8) | 0.0218 (8) | 0.0310 (9) | 0.0010 (6) | 0.0058 (7) | 0.0001 (7) |
| C3  | 0.0300 (8) | 0.0248 (8) | 0.0319 (9) | 0.0000 (7) | 0.0096 (7) | −0.0022 (7)|
| C4  | 0.0267 (8) | 0.0268 (9) | 0.0305 (9) | −0.0005 (7)| 0.0098 (7) | −0.0023 (7)|
| C5  | 0.0240 (8) | 0.0255 (8) | 0.0300 (9) | −0.0003 (6)| 0.0060 (6) | 0.0015 (7) |
| C6  | 0.0233 (7) | 0.0228 (8) | 0.0303 (8) | −0.0006 (6)| 0.0040 (6) | 0.0003 (7) |
| C7  | 0.0243 (8) | 0.0310 (9) | 0.0278 (8) | −0.0053 (7)| 0.0064 (6) | −0.0040 (7)|
| C8  | 0.0319 (9) | 0.0351 (10)| 0.0331 (9) | −0.0054 (8)| 0.0072 (7) | 0.0005 (8) |
| C9  | 0.0395 (10)| 0.0479 (12)| 0.0366 (10)| −0.0109 (9)| 0.0135 (8) | 0.0021 (9) |
| C10 | 0.0368 (10)| 0.0531 (13)| 0.0404 (11)| −0.0106 (9)| 0.0173 (9) | −0.0088 (10)|
| C11 | 0.0304 (9) | 0.0418 (11)| 0.0426 (11)| −0.0044 (8)| 0.0122 (8) | −0.0118 (9)|
| C12 | 0.0296 (9) | 0.0313 (9) | 0.0329 (9) | −0.0019 (7)| 0.0083 (7) | −0.0033 (8)|
| C13 | 0.0279 (8) | 0.0239 (8) | 0.0286 (8) | −0.0032 (6)| 0.0089 (7) | −0.0008 (7)|
| C14 | 0.0276 (8) | 0.0259 (8) | 0.0278 (8) | −0.0031 (7)| 0.0067 (7) | −0.0011 (7)|
| C15 | 0.0308 (8) | 0.0283 (9) | 0.0312 (9) | 0.0005 (7) | 0.0105 (7) | 0.0018 (7) |
| C16 | 0.0300 (9) | 0.0356 (10)| 0.0273 (9) | −0.0003 (7)| 0.0047 (7) | 0.0052 (7) |
| C17 | 0.0347 (9) | 0.0368 (10)| 0.0269 (9) | −0.0047 (8)| 0.0063 (7) | −0.0033 (8)|
| C18 | 0.0342 (9) | 0.0280 (9) | 0.0290 (9) | −0.0020 (7)| 0.0106 (7) | −0.0030 (7)|
| C19 | 0.0529 (13)| 0.0586 (15)| 0.0408 (12)| 0.0229 (12)| 0.0002 (10)| 0.0033 (11)|
| C20 | 0.0264 (8) | 0.0245 (8) | 0.0280 (8) | 0.0024 (7) | 0.0054 (6) | 0.0005 (7) |

### Geometric parameters (Å, °)

|     | C2—C19 | C8—H8  | C9—H9  | C10—C11 | C10—C11 | C10—C11 |
|-----|--------|--------|--------|---------|---------|---------|
| O1  | 1.214 (2) | 0.9500 | 1.385 (3) | 1.379 (3) | 0.9500 |
| O2  | 1.530 (2) | 0.9500 | 1.390 (3) | 1.391 (3) | 0.9500 |
| N1  | 1.050 (2) | 0.9500 | 1.080 (6) | 0.080 (6) | 0.080 (6) |
| N2  | 1.095 (2) | 0.9500 | 1.390 (3) | 1.391 (3) | 0.9500 |
| N3  | 1.050 (2) | 0.9500 | 1.080 (6) | 0.080 (6) | 0.080 (6) |
| N4  | 1.095 (2) | 0.9500 | 1.390 (3) | 1.391 (3) | 0.9500 |
| N5  | 1.050 (2) | 0.9500 | 1.080 (6) | 0.080 (6) | 0.080 (6) |
| N6  | 1.095 (2) | 0.9500 | 1.390 (3) | 1.391 (3) | 0.9500 |
| N7  | 1.050 (2) | 0.9500 | 1.080 (6) | 0.080 (6) | 0.080 (6) |
| N8  | 1.095 (2) | 0.9500 | 1.390 (3) | 1.391 (3) | 0.9500 |
| N9  | 1.050 (2) | 0.9500 | 1.080 (6) | 0.080 (6) | 0.080 (6) |
| N10 | 1.095 (2) | 0.9500 | 1.390 (3) | 1.391 (3) | 0.9500 |
| N11 | 1.050 (2) | 0.9500 | 1.080 (6) | 0.080 (6) | 0.080 (6) |
| N12 | 1.095 (2) | 0.9500 | 1.390 (3) | 1.391 (3) | 0.9500 |
| N13 | 1.050 (2) | 0.9500 | 1.080 (6) | 0.080 (6) | 0.080 (6) |
| N14 | 1.095 (2) | 0.9500 | 1.390 (3) | 1.391 (3) | 0.9500 |
| N15 | 1.050 (2) | 0.9500 | 1.080 (6) | 0.080 (6) | 0.080 (6) |
| N16 | 1.095 (2) | 0.9500 | 1.390 (3) | 1.391 (3) | 0.9500 |
supporting information

C3—H3A 0.9900  C15—C16 1.383 (3)
C3—H3B 0.9900  C15—H15 0.9500
C4—C5 1.508 (2)  C16—C17 1.395 (3)
C4—C13 1.529 (2)  C17—C18 1.381 (3)
C4—H4 1.0000  C17—H17 0.9500
C5—C6 1.365 (2)  C18—H18 0.9500
C5—C20 1.410 (2)  C19—H19A 0.9800
C7—C8 1.383 (3)  C19—H19B 0.9800
C7—C12 1.389 (3)  C19—H19C 0.9800
C8—C9 1.386 (3)

C16—O2—C19 116.44 (16)  C8—C9—H9 119.7
C2—N1—C6 121.62 (15)  C11—C10—C9 120.19 (19)
C2—N1—C7 118.78 (14)  C11—C10—H10 119.9
C6—N1—C7 119.55 (14)  C9—C10—H10 119.9
C6—N3—H3C 122.5 (15)  C10—C11—C12 119.9 (2)
C6—N3—H3D 117.7 (15)  C10—C11—H11 120.0
H3C—N3—H3D 118 (2)
O1—C2—N1 121.14 (16)  C7—C12—C11 119.35 (19)
O1—C2—C3 122.71 (16)  C7—C12—H12 120.3
N1—C2—C3 116.16 (15)  C7—C12—H12 120.3
C2—C3—C4 111.53 (14)  C14—C13—C18 117.78 (17)
C2—C3—H3A 109.3  C14—C13—C18 121.64 (16)
C4—C3—C4 109.3  C14—C13—C18 120.58 (16)
C4—C3—H3B 109.3  C13—C14—C15 122.01 (17)
C4—C3—H3B 109.3  C13—C14—H14 119.0
H3C—C3—H3B 108.0  C15—C14—H14 119.0
C5—C4—C13 114.33 (15)  C16—C15—C14 119.18 (17)
C5—C4—C3 106.59 (15)  C16—C15—H15 120.4
C13—C4—C3 111.84 (14)  C14—C15—H15 120.4
C5—C4—H4 108.0  O2—C16—C15 123.92 (18)
C13—C4—H4 108.0  O2—C16—C15 116.22 (17)
C3—C4—H4 108.0  C15—C16—C17 119.86 (17)
C6—C5—C20 119.33 (16)  C18—C17—C16 120.13 (17)
C6—C5—C4 120.46 (15)  C18—C17—H17 119.9
C20—C5—C4 120.21 (16)  C16—C17—H17 119.9
N3—C6—C5 124.45 (16)  C17—C18—C13 121.01 (18)
N3—C6—N1 116.48 (16)  C17—C18—H18 119.5
C5—C6—N1 119.07 (16)  C13—C18—H18 119.5
C8—C7—C12 121.01 (17)  O2—C19—H19A 109.5
C8—C7—N1 120.29 (17)  O2—C19—H19B 109.5
C12—C7—N1 118.68 (16)  H19A—C19—H19B 109.5
C7—C8—C9 118.95 (19)  O2—C19—H19C 109.5
C7—C8—H8 120.5  H19A—C19—H19C 109.5
C9—C8—H8 120.5  H19B—C19—H19C 109.5
C10—C9—C8 120.5 (2)  N2—C20—C5 178.6 (2)
C10—C9—H9 119.7

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C6—N1—C2—O1 −177.75 (16) C12—C7—C8—C9 −0.9 (3)
C7—N1—C2—O1 4.8 (3) N1—C7—C8—C9 177.59 (17)
C6—N1—C2—C3 2.1 (2) C7—C8—C9—C10 1.5 (3)
C7—N1—C2—C3 −175.40 (15) C8—C9—C10—C11 −0.8 (3)
N1—C2—C3—C4 36.8 (2) C9—C10—C11—C12 −0.6 (3)
C2—C3—C4—C5 −54.71 (18) N1—C7—C12—C11 −178.91 (16)
C2—C3—C4—C13 70.92 (19) C10—C11—C12—C7 1.1 (3)
C13—C4—C5—C6 −84.4 (2) C5—C4—C13—C14 7.1 (2)
C3—C4—C5—C6 39.7 (2) C3—C4—C13—C14 −114.15 (18)
C13—C4—C5—C20 95.23 (19) C5—C4—C13—C18 −172.53 (16)
C3—C4—C5—C20 −140.67 (16) C3—C4—C13—C18 66.2 (2)
C20—C5—C6—N3 −2.7 (3) C18—C13—C14—C15 1.7 (3)
C4—C5—C6—N3 176.95 (17) C4—C13—C14—C15 −177.99 (16)
C20—C5—C6—N1 177.30 (15) C13—C14—C15—C16 −1.4 (3)
C4—C5—C6—N1 −3.1 (2) C19—O2—C16—C15 −5.2 (3)
C2—N1—C6—N3 159.46 (16) C19—O2—C16—C17 174.22 (19)
C7—N1—C6—N3 −23.1 (2) C14—C15—C16—C17 179.53 (17)
C2—N1—C6—C5 −20.5 (2) C14—C15—C16—C18 0.1 (3)
C7—N1—C6—C5 156.97 (16) O2—C16—C17—C18 −178.57 (17)
C2—N1—C7—C8 −57.2 (2) C15—C16—C17—C18 0.9 (3)
C6—N1—C7—C8 125.25 (18) C16—C17—C18—C13 −0.6 (3)
C2—N1—C7—C12 121.29 (18) C14—C13—C18—C17 −0.6 (3)
C6—N1—C7—C12 −56.3 (2) C4—C13—C18—C17 179.03 (17)

Hydrogen-bond geometry (Å, °)

\( Cg_3 \) is the centroid of the C13–C18 benzene ring of the methoxyphenyl group.

| D—H···A | \( D—H \) | H···A | D···A | D—H···A |
|---------|-------|------|------|------|
| N3—H3C···N2i | 0.91 (2) | 2.10 (2) | 2.996 (2) | 166 (2) |
| N3—H3D···O2ii | 0.91 (2) | 2.48 (2) | 3.152 (2) | 131.0 (19) |
| C11—H11···O1ii | 0.95 | 2.55 | 3.210 (3) | 127 |
| C14—H14···O1iv | 0.95 | 2.48 | 3.199 (2) | 133 |
| C10—H10···Cg3iii | 0.95 | 2.99 | 3.813 (3) | 146 |
| C18—H18···Cg3v | 0.95 | 2.87 | 3.716 (2) | 150 |

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