Crystal structure of 2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-4H-chromene-3-carbonitrile

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In the title compound, C\textsubscript{22}H\textsubscript{20}N\textsubscript{2}O\textsubscript{2}, both six-membered rings of the fused heterocyclic system display envelope conformations; the two carbon atoms bearing the methyl groups and the naphthyl substituent both lie outside the planes of the other atoms of each ring. In the crystal, the amino group forms hydrogen bonds of the types N—H···O and N—H···N, leading to the formation of a double layer structure propagating parallel to the \textit{bc} plane. Weak C—H···O and C—H···\pi interactions may reinforce the layers.

1. Chemical context

Six-membered heterocycles involving 4\textit{H}-pyran units represent an important class of biologically active synthetic and natural products, many of which attract the interest of the drug industry (Le

Pyrans possess antimicrobial (Dazmiri \textit{et al.}, 2020), antituberculosis (Kalario \textit{et al.}, 2014) and antitumor (Wang \textit{et al.}, 2014) activities, whereby 4\textit{H}-pyrans are moieties in a series of natural products (Singh \textit{et al.}, 1996). A number of 4\textit{H}-pyrans are used, for example, as photoactive ingredients (Armesto \textit{et al.}, 1989) or agrochemicals (Kumar \textit{et al.}, 2009). Syntheticlly, they are intermediates for the synthesis of heterocyclic compounds such as pyranopyrimidines and pyranopyrazoles (Elgemeie \textit{et al.}, 1987, 1988) and consequently the synthesis of 4\textit{H}-pyrans themselves is of interest to organic chemists.

Some time ago, we reported the synthesis of pyridine-2(1\textit{H})-thiones and their condensed derivatives from the reactions of arylmethylenecyanothioacetamides with suitable active methylene compounds (Elgemeie \textit{et al.}, 2002). We also described the reaction of the dimedone 1 with naphthylmethylene cyanthioacetamide to produce a condensed pyridine-2(1\textit{H})-thione (Attia \textit{et al.}, 1997). The course of this reaction prompted us to investigate how 1 would react with naphthylmethylene cyanthioacetamide [2-cyano-3-(naphthalen-2-yl)acrylamide, 2] in boiling ethanol containing triethylamine. The product was shown to be neither of the expected condensed pyridin-2(1\textit{H})-ones 3 or 4 but rather the condensed pyran nitrile 5 (Scheme 1). The latter structure was inferred on the basis of elemental analysis and spectroscopic data: thus, the mass spectrum of 5 was compatible with the molecular formula C\textsubscript{22}H\textsubscript{20}N\textsubscript{2}O\textsubscript{2} (\textit{M}^+, 344), and the \textit{1H} NMR spectrum had signals at 4.37 (pyran-\textit{4H}), 7.06 (\textit{br}, NH\textsubscript{2}) and 7.29–7.90 (\textit{m}, ArH).
We assume that the formation of 5 proceeds via addition of the active methylene group of 1 to the double bond of 2 to give the intermediates 6, 7 and then 8, the latter finally losing one molecule of water to give the final product 5 (Scheme 2). In order to establish the structure of this compound unambiguously, its crystal structure was determined and is reported here.

2. Structural commentary

The molecular structure of 5 is shown in Fig. 1 and it confirms the postulated structure noted above. Both six-membered rings display envelope conformations in which five atoms are reasonably coplanar (for torsion angles see Table 1): C4 deviates by 0.317 (1) Å from the mean plane (I) of atoms O1/C2/C3/C4 (r.m.s. deviation = 0.031 Å), and C7 lies 0.653 (2) Å outside the mean plane (II) of C4/C5–C8 (r.m.s. deviation = 0.030 Å). The interplanar angle I/II is 9.97 (4)°. The naphthyl ring system (r.m.s. deviation = 0.012 Å) is effectively perpendicular to plane I [interplanar angle = 86.56 (3)°]. The amino group is almost planar (r.m.s. deviation of C2/N1/H01/H02 = 0.01 Å) and deviates slightly from plane I [interplanar angle = 10.0 (6)°].

Table 1
Selected torsion angles (°).

| Bond/Angle | Value (°) |
|------------|-----------|
| C8A–O1–C2–C3 | -8.36 (13) |
| O1–C2–C3–C4 | -9.65 (14) |
| C2–C3–C4–C4A | 22.65 (13) |
| C3–C4–C4A–C8A | -20.86 (12) |
| C8A–C4A–C5–C6 | 6.61 (14) |
| C4A–C5–C6–C7 | -31.83 (13) |
| C8A–O1–C8A–C4A | 54.40 (11) |
| O1–C8A–C4A–C8A | -47.78 (11) |
| C4A–C4A–C8A–C8A | 5.99 (15) |
| C5–C4A–C8A–C8A | 5.73 (15) |
| C8A–C8A–C5–C6 | 10.40 (13) |
| C4A–C5–C6–C7 | 19.52 (14) |

Figure 1
The molecular structure of 5 in the crystal. Ellipsoids represent 50% probability levels.
3. Supramolecular features

In the crystal, the amino group acts as donor for two classical hydrogen bonds (Table 2). This leads to a double layer structure (Fig. 2) propagating parallel to the bc plane. The H⋯O separation of the weak hydrogen bond C6—H6B⋯N2 (x, −1 + y, z) is rather long at 2.69 Å but acceptably linear (160°) and presumably reinforces the layer structure, but is not shown in Fig. 2. The short contact C10—H10B⋯Cg (C12–16/C21), with H⋯Cg 2.79 Å and a C—H⋯Cg angle of 139°, may represent a C—H⋯π interaction between the double layers. There are no short π⋯π stacking contacts.

4. Database survey

A search of the Cambridge Database (Version 2021.3.0; Groom et al., 2016) showed that the motif of a 4-substituted 2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4H-chromene-3-carbonitrile has been the subject of many structure determinations. A total of 54 hits with variously substituted phenyl groups was found, which reduces to 32 when duplicate structure determinations, various solvates and polymorphs are not considered. For all but one of these structures, the 4-position also bears a hydrogen atom, the exception being the 4-methyl, 4-nitrophenyl derivative (Cai et al., 2012; refcode TESNEM). Additionally, the 4-(1-naphthyl) derivative was found (Nesterov et al., 2004; refcode ETOKIH), which is an isomer of the title compound 5. The packing of ETOKIH is quite different from that of 5; the hydrogen atom corresponding to H01 in 5 forms N—H⋯N hydrogen bonds, leading to inversion dimers, whereas the other NH hydrogen atom is not involved in hydrogen bonding. A least-squares overlay of 5 and ETOKIH (excluding methyl groups and all naphthyl carbon atoms except the ipso C atom) gave an r.m.s. deviation of 0.15 Å; Fig. 3 shows the slight differences in ring conformation.

5. Synthesis and crystallization

A mixture of dimedone 1 (0.010 mol), 2-cyano-3-(naphthalen-2-yl)acrylamide 2 (0.010 mol) and triethylamine (0.010 mol) in ethanol (10 ml) was refluxed for 2 h. The solid precipitate that formed was filtered off and recrystallized from ethanol solution to give pale yellow crystals of 5 in 90% yield, m.p. 474–475 K; IR (KBr, cm⁻¹): ν 3345, 3258 (NH 2), 2188 (CN), 1683 (C=O). 1H NMR (400 MHz DMSO-d6): 1.11 (s, 3H, CH3), 1.53 (s, 3H, CH3), 2.07 (d, 2H, CH2), 2.14 (d, 2H, CH2), 4.37 (s, 1H, CH-pyran), 7.06 (s, br, 2H, NH2), 7.29–7.90 (m, 7H, C10H7). 13C NMR (100 MHz, DMSO-d6): δ: 27.2, 28.8, 32.2, 36.3, 50.4, 58.6 (aliphatic C), 120.2 (CN), 113.0, 142.2, 158.9, 163.0 (ethylene C), 120.2-133.3 (aromatic C), 196.2 (C=O).

Table 2

| D—H⋯A | D—H | H⋯A | D⋯A | D—H⋯A |
|-------|-----|-----|-----|-------|
| N1⋯H01⋯N2’ | 0.90 (1) | 2.11 (1) | 2.9948 (12) | 170 (1) |
| N1⋯H02⋯O2’ii | 0.90 (1) | 1.94 (1) | 2.8404 (11) | 176 (1) |
| C6⋯H6B⋯N2iii | 0.99 | 2.69 | 3.6366 (14) | 160 |

Symmetry codes: (i) x, y+1, z; (ii) x, y+1, z—1; (iii) x, y, z.

Figure 2

Crystal packing of 5 viewed parallel to the a axis in the region x ≈ 0.5. Dashed lines indicate classical hydrogen bonds. Naphthyl rings are reduced to the ipso carbon atoms for clarity. Hydrogen atoms not involved in classical hydrogen bonding are omitted. The figure is depth-coded; molecules of the lower layer are drawn with thinner bonds. Atom labels indicate the asymmetric unit (which lies in the lower layer).

Figure 3

A least-squares fit of 5 (violet, full bonds) to ETOKIH (Nesterov et al., 2004; green, dashed bonds). Hydrogen atoms were not considered.
MS (EI): m/z 344 [M⁺]. Analysis calculated for C_{22}H_{20}N_{2}O_{2}: C 76.72; H 5.85; N 8.13%. Found: C 76.6; H 5.7; N 8.1%.

6. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 3. The hydrogen atoms of the NH₂ group were refined freely, but with N—H distances restrained to be approximately equal using a SADI instruction in SHELXL. The methyl groups were included as idealised rigid groups allowed to rotate but not tip (C—H = 0.98 Å; H—C—H = 109.5°). The other hydrogen atoms were included using a riding model starting from calculated positions (C—H = 0.95 Å; H—C—H = 109.5°; iso(H) values were fixed at 1.5). The methyl groups were included as idealised rigid groups allowed to rotate but not tip (C—H = 0.98 Å; H—C—H = 109.5°). The other hydrogen atoms were included using a riding model starting from calculated positions (C—H = 0.95, 0.98 and 1.00 Å for aromatic, methylene and methine H atoms, respectively). The U(eq) values were fixed at 1.5 × U(eq) of the parent carbon atoms for the methyl groups and 1.2 × U(eq) for other hydrogen atoms.

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Table 3
Experimental details.

| Crystal data          | Chemical formula | C_{22}H_{20}N_{2}O_{2} |
|-----------------------|------------------|------------------------|
| M(r)                  |                  | 344.40                 |
| Crystal system, space group | Monoclinic, C2/c |
| Temperature (K)       |                  | 100                    |
| a (Å)                 |                  | 25.3144 (3), 9.25765 (11) |
| b (Å)                 |                  | 15.6778 (2)           |
| c (Å)                 |                  | 8                      |
| β (°)                 |                  | 97.8724 (10)          |
| V (Å³)                |                  | 3639.51 (8)           |
| Z                     |                  | 8                      |
| Radiation type        |                  | Cu Kα                 |
| μ (mm⁻¹)              |                  | 0.65                   |
| Crystal size (mm)     |                  | 0.08 × 0.05 × 0.02    |

Data collection
Diffractometer: XtaLAB Synergy, HyPix
Absorption correction: Multi-scan (CrysAlis PRO; Rigaku OD, 2021)
Tmin, Tmax: 0.826, 1.000
No. of measured, independent and observed [I > 2σ(I)] reflections: 61093, 3856, 3694
Rint: 0.030
(wR2)max: 0.634

Refinement
R[F² > 2σ(F²)], wR(F²), S: 0.036, 0.086, 1.07
No. of reflections: 3856
No. of parameters: 245
No. of restraints: 1
H-atom treatment: H atoms treated by a mixture of independent and constrained refinement
Δρmax, Δρmin (e Å⁻³): 0.22, −0.20

Computer programs: CrysAlis PRO (Rigaku OD, 2021). SHELXL (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b) and XP (Siemens, 1994).

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Crystal structure of 2-amino-5,6,7,8-tetrahydro-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-4H-chromene-3-carbonitrile

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Computing details
Data collection: CrysAlis PRO (Rigaku OD, 2021); cell refinement: CrysAlis PRO (Rigaku OD, 2021); data reduction: CrysAlis PRO (Rigaku OD, 2021); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015b); molecular graphics: XP (Siemens, 1994); software used to prepare material for publication: SHELXL2018/3 (Sheldrick, 2015b).

2-Amino-5,6,7,8-tetrahydro-7,7-dimethyl-4-(naphthalen-2-yl)-5-oxo-4H-chromene-3-carbonitrile

Crystal data
C_{22}H_{20}N_{2}O_{2}
Mr = 344.40
Monoclinic, C2/c
a = 25.3144 (3) Å
b = 9.25765 (11) Å
c = 15.6778 (2) Å
β = 97.8724 (10)°
V = 3639.51 (8) Å³
Z = 8

F(000) = 1456
D_{x} = 1.257 Mg m⁻³
Cu Kα radiation, λ = 1.54184 Å
Cell parameters from 35871 reflections
θ = 3.5–77.4°
µ = 0.65 mm⁻¹
T = 100 K
Lath, colourless
0.08 × 0.05 × 0.02 mm

Data collection
XtaLAB Synergy, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube
Detector resolution: 10.0000 pixels mm⁻¹
ω scans
Absorption correction: multi-scans
(CrystalisPro; Rigaku OD, 2021)
T_{min} = 0.826, T_{max} = 1.000

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.036
wR(F²) = 0.086
S = 1.07
3856 reflections
245 parameters
1 restraint
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(F²) + (0.0362P)² + 2.6486P]
where P = (F² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.22 e Å⁻³
Δρ_{min} = −0.20 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.

Least-squares planes (x,y,z in crystal coordinates) and deviations from them (* indicates atom used to define plane)
24.6913 (0.0028) x - 2.0266 (0.0045) y - 2.5063 (0.0065) z = 7.9737 (0.0050)
* -0.0099 (0.0006) C4A * -0.0265 (0.0007) C5 * 0.0300 (0.0005) C6 * -0.0353 (0.0005) C8 * 0.0417 (0.0007) C8A
-0.6525 (0.0015) C7
Rms deviation of fitted atoms = 0.0306
23.4020 (0.0039) x - 3.5289 (0.0034) y - 1.8463 (0.0073) z = 7.1162 (0.0054)
Angle to previous plane (with approximate esd) = 9.967 ( 0.036 )
* -0.0423 (0.0006) O1 * 0.0228 (0.0006) C2 * -0.0021 (0.0005) C3 * -0.0200 (0.0005) C4A * 0.0415 (0.0006) C8A
-0.3166 (0.0014) C4
Rms deviation of fitted atoms = 0.0298
- 6.0033 (0.0056) x - 6.6409 (0.0023) y + 10.6832 (0.0042) z = 0.1010 (0.0050)
Angle to previous plane (with approximate esd) = 86.556 ( 0.027 )
* -0.0188 (0.0008) C12 * -0.0048 (0.0008) C13 * 0.0149 (0.0009) C14 * 0.0098 (0.0010) C15 * -0.0015 (0.0011) C16 *
-0.0151 (0.0011) C17 * -0.0093 (0.0011) C18 * 0.0169 (0.0011) C19 * 0.0111 (0.0010) C20 * -0.0032 (0.0010) C21
Rms deviation of fitted atoms = 0.0119

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|   | x     | y     | z     | Uiso/Ueq |
|---|-------|-------|-------|----------|
| O1| 0.42046 (3) | 0.54277 (7) | 0.46059 (4) | 0.01878 (16) |
| C2| 0.44459 (4) | 0.67304 (10) | 0.48220 (6) | 0.01719 (19) |
| N1| 0.45324 (4) | 0.74447 (10) | 0.41141 (6) | 0.02197 (19) |
| H01| 0.4646 (6) | 0.8361 (15) | 0.4146 (9) | 0.038 (4)* |
| H02| 0.4446 (6) | 0.7028 (15) | 0.3594 (8) | 0.036 (4)* |
| C3| 0.45648 (4) | 0.71509 (10) | 0.56594 (6) | 0.0174 (2) |
| C4| 0.43643 (4) | 0.63303 (11) | 0.63906 (6) | 0.0175 (2) |
| H4| 0.465617 | 0.629568 | 0.688927 | 0.021* |
| C4A| 0.42383 (4) | 0.48120 (10) | 0.60884 (6) | 0.0172 (2) |
| C5| 0.42044 (4) | 0.36809 (11) | 0.67350 (6) | 0.0198 (2) |
| O2| 0.42982 (3) | 0.39810 (8) | 0.75024 (5) | 0.02716 (18) |
| C6| 0.40710 (4) | 0.21643 (11) | 0.64222 (7) | 0.0231 (2) |
| H6A| 0.389602 | 0.164811 | 0.686041 | 0.028* |
| H6B| 0.440604 | 0.164729 | 0.636056 | 0.028* |
| C7| 0.37033 (4) | 0.21205 (11) | 0.55576 (7) | 0.0223 (2) |
| C8| 0.39608 (4) | 0.30239 (11) | 0.49014 (6) | 0.0204 (2) |
| H8A| 0.426832 | 0.248784 | 0.473153 | 0.025* |
| H8B| 0.369856 | 0.316614 | 0.437883 | 0.025* |
| C8A| 0.41454 (4) | 0.44589 (10) | 0.52524 (6) | 0.01697 (19) |
| C9| 0.48381 (4) | 0.84661 (11) | 0.58446 (6) | 0.0183 (2) |
| N2| 0.50703 (4) | 0.95261 (10) | 0.60116 (6) | 0.0238 (2) |
| C10| 0.36359 (5) | 0.05655 (12) | 0.52270 (8) | 0.0311 (3) |
| H10A| 0.338967 | 0.055087 | 0.468724 | 0.047* |
| H10B| 0.349210 | -0.003296 | 0.565660 | 0.047* |
| H10C| 0.398300 | 0.018361 | 0.512555 | 0.047* |
| C11| 0.31556 (4) | 0.27340 (14) | 0.56747 (8) | 0.0312 (3) |
### Atomic displacement parameters (Å²)

|   | $U^{11}$   | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|---|------------|-----------|-----------|-----------|-----------|-----------|
| O1| 0.0252 (4) | 0.0155 (3) | 0.0155 (3) | -0.0050 (3) | 0.0022 (3) | 0.0003 (3) |
| C2| 0.0174 (4) | 0.0155 (4) | 0.0189 (5) | -0.0018 (3) | 0.0030 (3) | -0.0002 (4) |
| N1| 0.0322 (5) | 0.0182 (4) | 0.0159 (4) | -0.0071 (4) | 0.0049 (3) | -0.0012 (3) |
| C3| 0.0179 (4) | 0.0165 (5) | 0.0176 (5) | -0.0017 (4) | 0.0024 (3) | 0.0004 (4) |
| C4| 0.0204 (5) | 0.0176 (5) | 0.0141 (4) | -0.0018 (4) | 0.0005 (3) | 0.0008 (4) |
| C4A| 0.0162 (4) | 0.0164 (5) | 0.0190 (5) | 0.0003 (3) | 0.0025 (3) | 0.0014 (4) |
| C5| 0.0195 (5) | 0.0199 (5) | 0.0204 (5) | 0.0019 (4) | 0.0036 (4) | 0.0030 (4) |
| O2| 0.0386 (4) | 0.0249 (4) | 0.0177 (4) | 0.0001 (3) | 0.0028 (3) | 0.0039 (3) |
| C6| 0.0281 (5) | 0.0175 (5) | 0.0238 (5) | -0.0008 (4) | 0.0038 (4) | 0.0050 (4) |
| C7| 0.0246 (5) | 0.0179 (5) | 0.0247 (5) | -0.0042 (4) | 0.0042 (4) | 0.0025 (4) |
| C8| 0.0238 (5) | 0.0171 (5) | 0.0207 (5) | -0.0023 (4) | 0.0042 (4) | -0.0006 (4) |
| C8A| 0.0163 (4) | 0.0160 (4) | 0.0189 (5) | 0.0003 (3) | 0.0036 (3) | 0.0030 (4) |
| C9| 0.0196 (5) | 0.0203 (5) | 0.0148 (4) | 0.0007 (4) | 0.0023 (3) | 0.0008 (4) |
| N2| 0.0290 (5) | 0.0208 (4) | 0.0210 (4) | -0.0049 (4) | 0.0018 (3) | -0.0004 (3) |
| C10| 0.0423 (7) | 0.0197 (5) | 0.0308 (6) | -0.0092 (5) | 0.0036 (5) | 0.0022 (4) |
| C11| 0.0219 (5) | 0.0343 (6) | 0.0380 (6) | -0.0061 (5) | 0.0062 (5) | 0.0034 (5) |
| C12| 0.0256 (5) | 0.0172 (5) | 0.0188 (5) | 0.0001 (4) | 0.0054 (4) | 0.0007 (4) |
| C13| 0.0265 (5) | 0.0162 (5) | 0.0148 (4) | -0.0013 (4) | 0.0057 (4) | 0.0018 (4) |
| C14| 0.0361 (6) | 0.0251 (5) | 0.0183 (5) | -0.0046 (4) | 0.0041 (4) | -0.0030 (4) |
| C15| 0.0524 (7) | 0.0264 (6) | 0.0228 (5) | 0.0005 (5) | 0.0143 (5) | -0.0063 (4) |
| C16| 0.0433 (7) | 0.0259 (6) | 0.0274 (6) | 0.0071 (5) | 0.0193 (5) | 0.0043 (5) |
| C17| 0.0621 (9) | 0.0411 (8) | 0.0421 (7) | 0.0186 (7) | 0.0304 (7) | 0.0038 (6) |
| C18| 0.0496 (8) | 0.0577 (9) | 0.0551 (9) | 0.0287 (7) | 0.0329 (7) | 0.0181 (7) |
| C19| 0.0308 (7) | 0.0577 (9) | 0.0527 (8) | 0.0146 (6) | 0.0174 (6) | 0.0211 (7) |
### Geometric parameters (Å, °)

| Bond                  | Distance (Å) | Angle (°)   |
|-----------------------|--------------|-------------|
| O1—C2                 | 1.3733 (11)  | C17—C18     | 1.359 (2)   |
| O1—C8A                | 1.3769 (11)  | C18—C19     | 1.405 (2)   |
| C2—N1                 | 1.3355 (13)  | C19—C20     | 1.3724 (18) |
| C2—C3                 | 1.3628 (13)  | C20—C21     | 1.4172 (17) |
| C3—C9                 | 1.4109 (13)  | N1—H01      | 0.895 (13)  |
| C3—C4                 | 1.5193 (13)  | N1—H02      | 0.901 (13)  |
| C4—C4A                | 1.5035 (13)  | C4—H4       | 1.0000      |
| C4—C13                | 1.5278 (14)  | C6—H6A      | 0.9900      |
| C4A—C8A               | 1.3400 (14)  | C6—H6B      | 0.9900      |
| C4A—C5                | 1.4681 (13)  | C8—H8A      | 0.9900      |
| C5—O2                 | 1.2259 (13)  | C8—H8B      | 0.9900      |
| C5—C6                 | 1.5101 (14)  | C10—H10A    | 0.9800      |
| C6—C7                 | 1.5362 (15)  | C10—H10B    | 0.9800      |
| C7—C10                | 1.5316 (15)  | C10—H10C    | 0.9800      |
| C7—C11                | 1.5323 (15)  | C11—H11A    | 0.9800      |
| C7—C8                 | 1.5384 (14)  | C11—H11B    | 0.9800      |
| C8—C8A                | 1.4885 (13)  | C11—H11C    | 0.9800      |
| C9—N2                 | 1.1553 (13)  | C12—H12     | 0.9500      |
| C12—C13               | 1.3721 (14)  | C14—H14     | 0.9500      |
| C12—C21               | 1.4173 (14)  | C15—H15     | 0.9500      |
| C13—C14               | 1.4164 (14)  | C17—H17     | 0.9500      |
| C14—C15               | 1.3678 (17)  | C18—H18     | 0.9500      |
| C15—C16               | 1.4135 (18)  | C19—H19     | 0.9500      |
| C16—C21               | 1.4206 (17)  | C20—H20     | 0.9500      |
| C16—C17               | 1.4244 (17)  |             |             |

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\begin{align*}
C2—O1—C8A & = 118.69 (7) & C12—C21—C16 & = 118.93 (10) & \\
N1—C2—C3 & = 128.28 (9) & C2—N1—H01 & = 120.8 (9) & \\
N1—C2—O1 & = 110.35 (8) & C2—N1—H02 & = 119.5 (9) & \\
C3—C2—O1 & = 121.37 (9) & H01—N1—H02 & = 119.5 (13) & \\
C2—C3—C9 & = 118.82 (9) & C4A—C4—H4 & = 108.6 & \\
C2—C3—C4 & = 122.11 (9) & C3—C4—H4 & = 108.6 & \\
C9—C3—C4 & = 118.77 (8) & C13—C4—H4 & = 108.6 & \\
C4A—C4—C3 & = 107.94 (8) & C5—C6—H6A & = 109.0 & \\
C4A—C4—C13 & = 112.25 (8) & C7—C6—H6A & = 109.0 & \\
C3—C4—C13 & = 110.83 (8) & C5—C6—H6B & = 109.0 & \\
C8A—C4A—C5 & = 118.84 (9) & C7—C6—H6B & = 109.0 & \\
C8A—C4A—C4 & = 122.52 (9) & H6A—C6—H6B & = 107.8 & \\
C5—C4A—C4 & = 118.63 (8) & C8A—C8—H8A & = 109.2 & \\
O2—C5—C4A & = 119.62 (9) & C7—C8—H8A & = 109.2 & \\
O2—C5—C6 & = 122.28 (9) & C8A—C8—H8B & = 109.2 & \\
C4A—C5—C6 & = 118.07 (9) & C7—C8—H8B & = 109.2 & \\
C5—C6—C7 & = 113.12 (8) & H8A—C8—H8B & = 107.9 & \\
\end{align*}
\]
C10—C7—C11       109.17 (9)  C7—C10—H10A       109.5
C10—C7—C6         110.45 (9)  C7—C10—H10B       109.5
C11—C7—C6         109.48 (9)  H10A—C10—H10B      109.5
C10—C7—C8         108.80 (9)  C7—C10—H10C       109.5
C11—C7—C8         110.60 (9)  H10A—C10—H10C      109.5
C6—C7—C8          108.34 (8)  C7—C10—H10D       109.5
C8A—C8—C7         112.23 (8)  C7—C11—H11A       109.5
C4A—C8A—O1        122.61 (9)  C7—C11—H11B       109.5
C4A—C8A—C8        125.70 (9)  H11A—C11—H11B      109.5
O1—C8A—C8         111.69 (8)  C7—C11—H11C       109.5
N2—C9—C3          178.34 (11) H11A—C11—H11C      109.5
C13—C12—C21       121.76 (10) C7—C11—H11D       109.5
C12—C13—C14       118.75 (10) C13—C12—H12       119.1
C12—C13—C4        121.77 (9)  C21—C12—H12       119.1
C14—C13—C4        119.37 (9)  C15—C14—H14       119.5
C15—C14—C13       120.90 (11) C13—C14—H14       119.5
C14—C15—C16       121.22 (11) C14—C15—H15       119.4
C15—C16—C21       118.42 (10) C16—C15—H15       119.4
C15—C16—C17       123.10 (12) C18—C17—H17       119.4
C21—C16—C17       118.48 (13) C16—C17—H17       119.4
C18—C17—C16       121.23 (14) C17—C18—H18       119.9
C17—C18—C19       120.17 (12) C19—C18—H18       119.9
C20—C19—C18       120.53 (14) C20—C19—H19       119.7
C19—C20—C21       120.63 (13) C18—C19—H19       119.7
C20—C21—C12       122.14 (11) C19—C20—H20       119.7
C20—C21—C16       118.93 (11) C21—C20—H20       119.7
C8A—O1—C2—N1      171.82 (8)  C4—C4A—C8A—C8     -172.89 (9)
C8A—O1—C2—C3      -8.36 (13)  C2—O1—C8A—C4A      10.40 (13)
N1—C2—C3—C9       -3.54 (16)  C2—O1—C8A—C8       -170.59 (8)
O1—C2—C3—C9       176.67 (9)  C7—C8—C8A—C4A      19.52 (14)
N1—C2—C3—C4       170.13 (10) C7—C8—C8A—O1      -159.46 (8)
O1—C2—C3—C4       -9.65 (14)  C21—C12—C13—C14    -0.51 (15)
C2—C3—C4—C4A      22.65 (13)  C21—C12—C13—C4     -176.64 (9)
C9—C3—C4—C4A      -163.67 (8) C4A—C4—C13—C12     -37.80 (12)
C2—C3—C4—C13      -100.65 (11) C3—C4—C13—C12    82.98 (11)
C9—C3—C4—C13      73.03 (11)  C4A—C4—C13—C14    146.09 (9)
C3—C4—C4A—C8A     -20.86 (12) C3—C4—C13—C14    -93.12 (11)
C13—C4—C4A—C8A    101.57 (11) C12—C13—C14—C15   -0.50 (16)
C3—C4—C4A—C5      160.51 (8)  C4—C13—C14—C15    175.72 (10)
C13—C4—C4A—C5     -77.05 (11) C13—C14—C15—C16   0.66 (17)
C8A—C4A—C5—O2     178.62 (9)  C14—C15—C16—C21   0.19 (17)
C4—C4A—C5—O2     -2.71 (14)  C14—C15—C16—C17   -179.62 (12)
C8A—C4A—C5—C6     0.61 (14)  C15—C16—C17—C18   -179.19 (13)
C4—C4A—C5—C6     179.28 (8)  C21—C16—C17—C18   0.99 (19)
O2—C5—C6—C7       150.21 (10) C16—C17—C18—C19  0.3 (2)
C4A—C5—C6—C7     -31.83 (13) C17—C18—C19—C20  -1.2 (2)
C5—C6—C7—C10      173.48 (9)  C18—C19—C20—C21   0.8 (2)
|                  |       |                  |       |                  |
|------------------|-------|------------------|-------|------------------|
| C5—C6—C7—C11    | −66.28 (11) | C19—C20—C21—C12 | −179.56 (11) |
| C5—C6—C7—C8     | 54.40 (11)  | C19—C20—C21—C16 | 0.47 (17)   |
| C10—C7—C8—C8A   | −167.89 (9) | C13—C12—C21—C20 | −178.63 (10) |
| C11—C7—C8—C8A   | 72.21 (11)  | C13—C12—C21—C16 | 1.34 (15)   |
| C6—C7—C8—C8A    | −47.78 (11) | C15—C16—C21—C20 | 178.82 (10) |
| C5—C4A—C8A—O1   | −175.40 (8) | C17—C16—C21—C20 | −1.36 (16)  |
| C4—C4A—C8A—O1   | 5.99 (15)   | C15—C16—C21—C12 | −1.16 (16)  |
| C5—C4A—C8A—C8   | 5.73 (15)   | C17—C16—C21—C12 | 178.66 (10) |

Hydrogen-bond geometry (Å, °)

| D—H···A         | D—H   | H···A   | D···A  | D—H···A |
|------------------|-------|--------|-------|---------|
| N1—H01···N2i     | 0.90 (1) | 2.11 (1) | 2.9948 (12) | 170 (1) |
| N1—H02···O2ii    | 0.90 (1) | 1.94 (1) | 2.8404 (11) | 176 (1) |
| C6—H6B···N2iii   | 0.99   | 2.69   | 3.6366 (14) | 160 |

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