# organic compounds

# Ethyl 2-amino-7,7-dimethyl-2′,5-dioxospiro[5,6,7,8-tetrahydro-4*H*-chromene-4,3′(2′*H*)-1*H*-indole]-3-carboxylate

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In the molecule of the title compound, $C_{21}H_{22}N_2O_5$, the indole system and the spiro-pyran ring are almost planar [maximum deviations of 0.0447 (17) and 0.0781 (17) Å, respectively]; the dihedral angle between them is 84.6 (3)°. The remaining six-membered ring adopts a twisted conformation. Intramolecular N—H⋯O hydrogen bonds occur. In the crystal structure, intermolecular N—H⋯O and C—H⋯O hydrogen bonds link the molecules.

## Related literature

For the indole nucleus, see: da Silva *et al.*, (2001). For the antibacterial and fungicidal activities of indoles, see: Joshi & Chand (1982). Spirooxindole ring systems are found in a number of alkaloids, see: Abdel-Rahman *et al.* (2004). For our work on the preparation of heterocyclic compounds involving indole derivatives, see: Zhu *et al.* (2007). For puckering parameters, see: Cremer & Pople (1975).
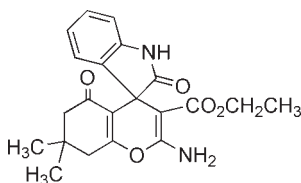


## Experimental

### Crystal data

| | |
|---|---|
| $C_{21}H_{22}N_2O_5$ | $V$ = 1849.2 (5) Å$^3$ |
| $M_r$ = 382.41 | $Z$ = 4 |
| Monoclinic, $P2_1/n$ | Mo $K\alpha$ radiation |
| $a$ = 8.4298 (14) Å | $\mu$ = 0.10 mm$^{-1}$ |
| $b$ = 11.6791 (17) Å | $T$ = 153 K |
| $c$ = 19.024 (3) Å | 0.50 × 0.35 × 0.12 mm |
| $\beta$ = 99.136 (4)° | |

### Data collection

| | |
|---|---|
| Rigaku Mercury diffractometer | 17728 measured reflections |
| Absorption correction: multi-scan (Jacobson, 1998) | 3374 independent reflections |
| $T_{min}$ = 0.814, $T_{max}$ = 0.988 | 2944 reflections with $I > 2\sigma(I)$ |
| | $R_{int}$ = 0.041 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.049 | 257 parameters |
| $wR(F^2)$ = 0.107 | H-atom parameters constrained |
| $S$ = 1.15 | $\Delta\rho_{max}$ = 0.20 e Å$^{-3}$ |
| 3374 reflections | $\Delta\rho_{min}$ = −0.23 e Å$^{-3}$ |

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

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| N1—H1$A$⋯O4 | 0.88 | 2.03 | 2.658 (2) | 128 |
| N1—H1$B$⋯O3$^i$ | 0.88 | 1.92 | 2.794 (2) | 175 |
| N2—H2⋯O2$^{ii}$ | 0.88 | 2.04 | 2.8435 (19) | 152 |
| C16—H16⋯O4$^{iii}$ | 0.95 | 2.54 | 3.448 (2) | 159 |

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

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPII* (Johnson, 1976) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DS2016).

## References

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# supporting information

# Ethyl 2-amino-7,7-dimethyl-2′,5-dioxospiro[5,6,7,8-tetrahydro-4*H*-chromene-4,3′(2′*H*)-1*H*-indole]-3-carboxylate

**Jing Wang and Song-Lei Zhu**

## S1. Comment

The indole nucleus is the well known heterocycle (da Silva *et al.*, 2001). Compounds carrying the indole moiety exhibit antibacterial and fungicidal activities (Joshi & Chand, 1982). Spirooxindole ring systems are found in a number of alkaloids like horsifiline, spirotryprostatin and elacomine (Abdel-Rahman *et al.*, 2004). As a part of our programme devoted to the preparation of heterocyclic compounds involving indole derivatives (Zhu *et al.*, 2007), we have synthesized a series of spirooxindoles *via* reactions of substituted isatins together with malononitrile (or ethyl 2-cyano-acetate) and enaminones . We report herein the crystal structure of the title compound, (I).

In the molecule of (I), (Fig. 1), the indole ring A (C3/C12/N2/C13-C18) and the spiro pyran ring B (O1/C1-C5), are planar. The dihedral angle between them is 84.6 (3)°. Ring C (C1/C2/C6-C9) adopts twisted conformation, with C7 and C8 deviating the C1/C2/C6/C9 plane by 0.1525 (18) and -0.4751 (18)Å, respectively. And the C1/C2/C6/C9 plane is oriented at a dihedral angle of 6.2 (2)° with the fused pyran ring B.

In the crystal structure, intermolecular and intramolecular N-H···O hydrogen bonds (N1-H1A···O4, N1-H1B···O3, N2-H2···O2. ) (Table 1) link the molecules (Fig. 2), in which they may be effective in the stabilization of the structure.

## S2. Experimental

Compound (I) was prepared by one-pot reaction of isatin (2 mmol), ethyl 2-cyanoacetate (2 mmol) and 5,5-dimethyl-cyclohexane- 1,3-dione (2 mmol) in water (10 ml). The reaction was catalyzed by TEBAC (triethylbenzylammonium chloride, 1 mmol). After stirring at 333 K for 5 h, the reaction mixture was cooled and washed with small amount of ethanol. The crude product was filtered and single crystals of the title compound were obtained from ethanol solution by slow evaporation at room temperature (yield; 80%, m.p. 518-519 K). Spectroscopic analysis: IR (KBr, n, cm$^{-1}$): 3364, 3241, 3187, 2955, 1690, 1613, 1520, 1474, 1304, 1227, 1165, 1057, 926, 748, 609, 556. $^1$H NMR (400 MHz, CDCl$_3$): 7.48 (br s, 1H, NH), 7.14 (t, J = 7.2 Hz, 1H, ArH), 6,88-6.94 (m, 2H, ArH), 6.80 (t, J = 8.4 Hz, 1H, ArH), 6.49 (br s, 2H, NH$_2$), 3.90-3.95 (m, 2H, CH$_2$), 2.51-2.54 (m, 2H, CH$_2$), 2.11-2.24 (m, 2H, CH$_2$), 1.28 (t, J = 7.6 Hz, 3H, CH$_3$), 1.10 (s, 3H, CH$_3$), 1.01(s, 3H, CH$_3$).

## S3. Refinement

H atoms were positioned geometrically, with N-H = 0.88 Å (for NH) and C-H = 0.95 and 0.98 Å for aromatic and methyl H, respectivly and constrained to ride on their parent atoms with U$_{iso}$(H) = xU$_{eq}$(C,N), where x = 1.5 for methyl H and x = 1.2 for all other H atoms.
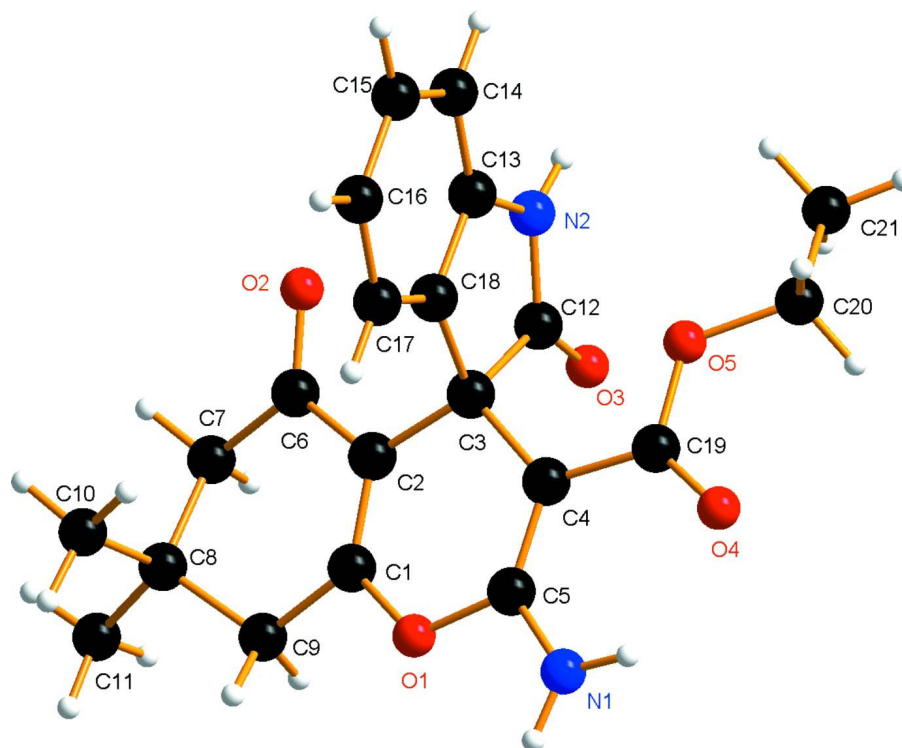
**Figure 1**

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
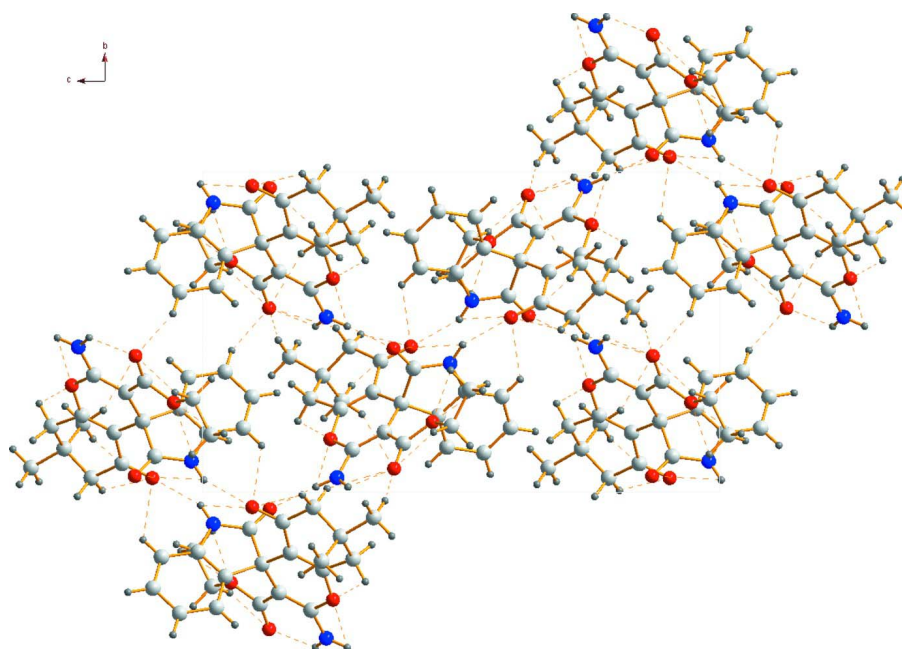
**Figure 2**

A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

**Ethyl 2-amino-7,7-dimethyl-2′,5-dioxospiro[5,6,7,8- tetrahydro-4H-chromene-4,3′(2′H)-1H-indole]-3-carboxylate**

*Crystal data*

| | |
|---|---|
| $C_{21}H_{22}N_2O_5$ | $F(000) = 808$ |
| $M_r = 382.41$ | $D_x = 1.374$ Mg m$^{-3}$ |
| Monoclinic, $P2_1/n$ | Melting point = 518–519 K |
| Hall symbol: -P 2yn | Mo $K\alpha$ radiation, $\lambda = 0.71070$ Å |
| $a = 8.4298$ (14) Å | Cell parameters from 6298 reflections |
| $b = 11.6791$ (17) Å | $\theta = 3.0$–$25.3°$ |
| $c = 19.024$ (3) Å | $\mu = 0.10$ mm$^{-1}$ |
| $\beta = 99.136$ (4)° | $T = 153$ K |
| $V = 1849.2$ (5) Å$^3$ | Block, colorless |
| $Z = 4$ | $0.50 \times 0.35 \times 0.12$ mm |

*Data collection*

| | |
|---|---|
| Rigaku Mercury diffractometer | 17728 measured reflections |
| Radiation source: fine-focus sealed tube | 3374 independent reflections |
| Graphite monochromator | 2944 reflections with $I > 2\sigma(I)$ |
| Detector resolution: 7.31 pixels mm$^{-1}$ | $R_{int} = 0.041$ |
| $\omega$ scans | $\theta_{max} = 25.4°$, $\theta_{min} = 3.0°$ |
| Absorption correction: multi-scan (Jacobson, 1998) | $h = -10 \rightarrow 10$ |
| | $k = -14 \rightarrow 13$ |
| $T_{min} = 0.814$, $T_{max} = 0.988$ | $l = -22 \rightarrow 22$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | |
| $R[F^2 > 2\sigma(F^2)] = 0.049$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.107$ | |
| $S = 1.15$ | H-atom parameters constrained |
| 3374 reflections | $w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.757P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| 257 parameters | |
| 0 restraints | $(\Delta/\sigma)_{max} < 0.001$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{max} = 0.20$ e Å$^{-3}$ |
| | $\Delta\rho_{min} = -0.23$ 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 F$^2$. The threshold expression of F$^2$ > 2sigma(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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.58254 (15) | 0.33374 (11) | 0.25244 (6) | 0.0258 (3) |
| O2 | 0.34545 (16) | 0.04523 (12) | 0.09660 (7) | 0.0315 (3) |

| | | | |
|---|---|---|---|
| O3 | 0.76243 (15) | 0.05137 (11) | 0.13053 (7) | 0.0271 (3) |
| O4 | 0.93311 (15) | 0.42547 (11) | 0.12924 (7) | 0.0276 (3) |
| O5 | 0.84779 (15) | 0.28028 (12) | 0.05510 (7) | 0.0290 (3) |
| N1 | 0.7795 (2) | 0.45339 (14) | 0.23971 (9) | 0.0323 (4) |
| H1A | 0.8561 | 0.4825 | 0.2187 | 0.039* |
| H1B | 0.7603 | 0.4822 | 0.2803 | 0.039* |
| N2 | 0.62096 (18) | 0.09772 (13) | 0.02113 (8) | 0.0220 (3) |
| H2 | 0.6506 | 0.0396 | −0.0032 | 0.026* |
| C1 | 0.4876 (2) | 0.24020 (15) | 0.23304 (9) | 0.0213 (4) |
| C2 | 0.4815 (2) | 0.18729 (15) | 0.17020 (9) | 0.0200 (4) |
| C3 | 0.5860 (2) | 0.22220 (15) | 0.11542 (9) | 0.0200 (4) |
| C4 | 0.7072 (2) | 0.31183 (15) | 0.14793 (9) | 0.0209 (4) |
| C5 | 0.6927 (2) | 0.36589 (16) | 0.21015 (9) | 0.0229 (4) |
| C6 | 0.3686 (2) | 0.09070 (16) | 0.15531 (10) | 0.0226 (4) |
| C7 | 0.2872 (2) | 0.04575 (16) | 0.21471 (10) | 0.0255 (4) |
| H7A | 0.3577 | −0.0125 | 0.2415 | 0.031* |
| H7B | 0.1864 | 0.0070 | 0.1936 | 0.031* |
| C8 | 0.2471 (2) | 0.13669 (16) | 0.26702 (9) | 0.0231 (4) |
| C9 | 0.3984 (2) | 0.20711 (17) | 0.29162 (10) | 0.0256 (4) |
| H9A | 0.3679 | 0.2775 | 0.3152 | 0.031* |
| H9B | 0.4710 | 0.1624 | 0.3275 | 0.031* |
| C10 | 0.1122 (2) | 0.21397 (18) | 0.23047 (11) | 0.0316 (5) |
| H10A | 0.1494 | 0.2558 | 0.1915 | 0.047* |
| H10B | 0.0818 | 0.2686 | 0.2651 | 0.047* |
| H10C | 0.0189 | 0.1670 | 0.2114 | 0.047* |
| C11 | 0.1937 (2) | 0.07742 (18) | 0.33125 (10) | 0.0309 (5) |
| H11A | 0.0951 | 0.0339 | 0.3155 | 0.046* |
| H11B | 0.1734 | 0.1352 | 0.3661 | 0.046* |
| H11C | 0.2784 | 0.0253 | 0.3532 | 0.046* |
| C12 | 0.6698 (2) | 0.11300 (15) | 0.09176 (9) | 0.0213 (4) |
| C13 | 0.5176 (2) | 0.18514 (15) | −0.00876 (9) | 0.0215 (4) |
| C14 | 0.4506 (2) | 0.20069 (17) | −0.07895 (10) | 0.0279 (5) |
| H14 | 0.4678 | 0.1471 | −0.1145 | 0.033* |
| C15 | 0.3570 (2) | 0.29760 (18) | −0.09573 (11) | 0.0324 (5) |
| H15 | 0.3084 | 0.3103 | −0.1437 | 0.039* |
| C16 | 0.3332 (2) | 0.37610 (18) | −0.04389 (11) | 0.0319 (5) |
| H16 | 0.2705 | 0.4427 | −0.0567 | 0.038* |
| C17 | 0.4006 (2) | 0.35815 (16) | 0.02711 (10) | 0.0261 (4) |
| H17 | 0.3839 | 0.4116 | 0.0629 | 0.031* |
| C18 | 0.4919 (2) | 0.26158 (15) | 0.04424 (9) | 0.0206 (4) |
| C19 | 0.8378 (2) | 0.34677 (16) | 0.11166 (9) | 0.0226 (4) |
| C20 | 0.9853 (2) | 0.29242 (19) | 0.01860 (11) | 0.0353 (5) |
| H20A | 1.0827 | 0.3117 | 0.0529 | 0.042* |
| H20B | 0.9661 | 0.3540 | −0.0175 | 0.042* |
| C21 | 1.0062 (3) | 0.1792 (2) | −0.01643 (12) | 0.0434 (6) |
| H21A | 1.0244 | 0.1191 | 0.0199 | 0.065* |
| H21B | 1.0986 | 0.1833 | −0.0417 | 0.065* |
| H21C | 0.9091 | 0.1615 | −0.0503 | 0.065* |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0258 (7) | 0.0279 (7) | 0.0249 (7) | −0.0071 (6) | 0.0076 (5) | −0.0071 (6) |
| O2 | 0.0358 (8) | 0.0318 (8) | 0.0291 (8) | −0.0101 (6) | 0.0120 (6) | −0.0115 (6) |
| O3 | 0.0269 (7) | 0.0275 (7) | 0.0271 (7) | 0.0066 (6) | 0.0047 (6) | 0.0049 (6) |
| O4 | 0.0237 (7) | 0.0265 (7) | 0.0321 (7) | −0.0066 (6) | 0.0031 (6) | 0.0005 (6) |
| O5 | 0.0266 (7) | 0.0351 (8) | 0.0275 (7) | −0.0099 (6) | 0.0117 (6) | −0.0045 (6) |
| N1 | 0.0331 (10) | 0.0342 (10) | 0.0308 (9) | −0.0124 (8) | 0.0087 (7) | −0.0130 (8) |
| N2 | 0.0249 (8) | 0.0209 (8) | 0.0213 (8) | −0.0001 (7) | 0.0074 (6) | −0.0028 (6) |
| C1 | 0.0190 (9) | 0.0216 (10) | 0.0230 (9) | −0.0001 (7) | 0.0024 (7) | −0.0002 (8) |
| C2 | 0.0192 (9) | 0.0202 (10) | 0.0212 (9) | 0.0000 (7) | 0.0049 (7) | 0.0006 (7) |
| C3 | 0.0193 (9) | 0.0198 (9) | 0.0211 (9) | −0.0006 (7) | 0.0040 (7) | −0.0015 (7) |
| C4 | 0.0197 (9) | 0.0204 (10) | 0.0223 (9) | −0.0003 (7) | 0.0020 (7) | 0.0006 (7) |
| C5 | 0.0202 (9) | 0.0247 (10) | 0.0235 (10) | −0.0015 (8) | 0.0024 (8) | −0.0001 (8) |
| C6 | 0.0214 (9) | 0.0205 (10) | 0.0266 (10) | 0.0026 (8) | 0.0061 (8) | −0.0024 (8) |
| C7 | 0.0255 (10) | 0.0232 (10) | 0.0291 (10) | −0.0012 (8) | 0.0082 (8) | 0.0007 (8) |
| C8 | 0.0212 (9) | 0.0241 (10) | 0.0253 (10) | 0.0019 (8) | 0.0072 (8) | 0.0026 (8) |
| C9 | 0.0261 (10) | 0.0285 (11) | 0.0229 (10) | 0.0035 (8) | 0.0066 (8) | 0.0001 (8) |
| C10 | 0.0237 (10) | 0.0332 (12) | 0.0383 (12) | 0.0061 (9) | 0.0062 (9) | 0.0047 (9) |
| C11 | 0.0317 (11) | 0.0330 (12) | 0.0308 (11) | 0.0012 (9) | 0.0134 (9) | 0.0045 (9) |
| C12 | 0.0207 (9) | 0.0203 (10) | 0.0242 (10) | −0.0039 (8) | 0.0073 (8) | 0.0009 (8) |
| C13 | 0.0189 (9) | 0.0239 (10) | 0.0220 (9) | −0.0050 (8) | 0.0047 (7) | 0.0005 (8) |
| C14 | 0.0280 (10) | 0.0342 (11) | 0.0218 (10) | −0.0088 (9) | 0.0051 (8) | 0.0005 (8) |
| C15 | 0.0267 (11) | 0.0413 (13) | 0.0270 (11) | −0.0059 (9) | −0.0021 (8) | 0.0092 (9) |
| C16 | 0.0238 (10) | 0.0308 (11) | 0.0391 (12) | 0.0014 (9) | −0.0005 (9) | 0.0122 (9) |
| C17 | 0.0212 (10) | 0.0239 (10) | 0.0333 (11) | −0.0017 (8) | 0.0045 (8) | 0.0001 (8) |
| C18 | 0.0175 (9) | 0.0209 (10) | 0.0235 (9) | −0.0042 (7) | 0.0039 (7) | 0.0006 (7) |
| C19 | 0.0212 (9) | 0.0235 (10) | 0.0219 (9) | −0.0001 (8) | −0.0003 (7) | 0.0032 (8) |
| C20 | 0.0305 (11) | 0.0459 (13) | 0.0333 (11) | −0.0100 (10) | 0.0167 (9) | −0.0016 (10) |
| C21 | 0.0393 (13) | 0.0514 (15) | 0.0449 (13) | −0.0047 (11) | 0.0229 (11) | −0.0058 (11) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.370 (2) | C8—C10 | 1.530 (3) |
| O1—C5 | 1.374 (2) | C8—C11 | 1.533 (3) |
| O2—C6 | 1.224 (2) | C9—H9A | 0.9900 |
| O3—C12 | 1.220 (2) | C9—H9B | 0.9900 |
| O4—C19 | 1.232 (2) | C10—H10A | 0.9800 |
| O5—C19 | 1.340 (2) | C10—H10B | 0.9800 |
| O5—C20 | 1.450 (2) | C10—H10C | 0.9800 |
| N1—C5 | 1.328 (2) | C11—H11A | 0.9800 |
| N1—H1A | 0.8800 | C11—H11B | 0.9800 |
| N1—H1B | 0.8800 | C11—H11C | 0.9800 |
| N2—C12 | 1.353 (2) | C13—C14 | 1.377 (3) |
| N2—C13 | 1.403 (2) | C13—C18 | 1.389 (3) |
| N2—H2 | 0.8800 | C14—C15 | 1.387 (3) |
| C1—C2 | 1.339 (2) | C14—H14 | 0.9500 |

| | | | |
|---|---|---|---|
| C1—C9 | 1.491 (3) | C15—C16 | 1.384 (3) |
| C2—C6 | 1.474 (3) | C15—H15 | 0.9500 |
| C2—C3 | 1.523 (2) | C16—C17 | 1.396 (3) |
| C3—C4 | 1.524 (2) | C16—H16 | 0.9500 |
| C3—C18 | 1.528 (2) | C17—C18 | 1.375 (3) |
| C3—C12 | 1.559 (3) | C17—H17 | 0.9500 |
| C4—C5 | 1.364 (3) | C20—C21 | 1.503 (3) |
| C4—C19 | 1.448 (3) | C20—H20A | 0.9900 |
| C6—C7 | 1.507 (3) | C20—H20B | 0.9900 |
| C7—C8 | 1.530 (3) | C21—H21A | 0.9800 |
| C7—H7A | 0.9900 | C21—H21B | 0.9800 |
| C7—H7B | 0.9900 | C21—H21C | 0.9800 |
| C8—C9 | 1.527 (3) | | |
| | | | |
| C1—O1—C5 | 118.72 (14) | C8—C10—H10B | 109.5 |
| C19—O5—C20 | 119.01 (15) | H10A—C10—H10B | 109.5 |
| C5—N1—H1A | 120.0 | C8—C10—H10C | 109.5 |
| C5—N1—H1B | 120.0 | H10A—C10—H10C | 109.5 |
| H1A—N1—H1B | 120.0 | H10B—C10—H10C | 109.5 |
| C12—N2—C13 | 112.20 (15) | C8—C11—H11A | 109.5 |
| C12—N2—H2 | 123.9 | C8—C11—H11B | 109.5 |
| C13—N2—H2 | 123.9 | H11A—C11—H11B | 109.5 |
| C2—C1—O1 | 123.13 (16) | C8—C11—H11C | 109.5 |
| C2—C1—C9 | 126.52 (17) | H11A—C11—H11C | 109.5 |
| O1—C1—C9 | 110.34 (15) | H11B—C11—H11C | 109.5 |
| C1—C2—C6 | 117.18 (16) | O3—C12—N2 | 125.94 (17) |
| C1—C2—C3 | 122.87 (16) | O3—C12—C3 | 125.73 (16) |
| C6—C2—C3 | 119.95 (15) | N2—C12—C3 | 108.32 (15) |
| C2—C3—C4 | 109.24 (14) | C14—C13—C18 | 122.13 (18) |
| C2—C3—C18 | 114.32 (14) | C14—C13—N2 | 128.45 (17) |
| C4—C3—C18 | 111.93 (14) | C18—C13—N2 | 109.39 (15) |
| C2—C3—C12 | 108.45 (14) | C13—C14—C15 | 117.47 (18) |
| C4—C3—C12 | 111.94 (14) | C13—C14—H14 | 121.3 |
| C18—C3—C12 | 100.71 (14) | C15—C14—H14 | 121.3 |
| C5—C4—C19 | 117.57 (16) | C16—C15—C14 | 121.19 (18) |
| C5—C4—C3 | 121.57 (16) | C16—C15—H15 | 119.4 |
| C19—C4—C3 | 120.78 (15) | C14—C15—H15 | 119.4 |
| N1—C5—C4 | 127.17 (17) | C15—C16—C17 | 120.47 (19) |
| N1—C5—O1 | 109.90 (15) | C15—C16—H16 | 119.8 |
| C4—C5—O1 | 122.93 (16) | C17—C16—H16 | 119.8 |
| O2—C6—C2 | 120.78 (16) | C18—C17—C16 | 118.64 (18) |
| O2—C6—C7 | 120.50 (17) | C18—C17—H17 | 120.7 |
| C2—C6—C7 | 118.66 (16) | C16—C17—H17 | 120.7 |
| C6—C7—C8 | 114.84 (16) | C17—C18—C13 | 120.07 (17) |
| C6—C7—H7A | 108.6 | C17—C18—C3 | 130.49 (17) |
| C8—C7—H7A | 108.6 | C13—C18—C3 | 109.33 (15) |
| C6—C7—H7B | 108.6 | O4—C19—O5 | 121.92 (17) |
| C8—C7—H7B | 108.6 | O4—C19—C4 | 126.41 (17) |

| | | | |
|---|---|---|---|
| H7A—C7—H7B | 107.5 | O5—C19—C4 | 111.66 (15) |
| C9—C8—C7 | 108.25 (15) | O5—C20—C21 | 106.56 (16) |
| C9—C8—C10 | 110.24 (16) | O5—C20—H20A | 110.4 |
| C7—C8—C10 | 109.82 (16) | C21—C20—H20A | 110.4 |
| C9—C8—C11 | 109.61 (15) | O5—C20—H20B | 110.4 |
| C7—C8—C11 | 109.16 (15) | C21—C20—H20B | 110.4 |
| C10—C8—C11 | 109.72 (15) | H20A—C20—H20B | 108.6 |
| C1—C9—C8 | 113.97 (15) | C20—C21—H21A | 109.5 |
| C1—C9—H9A | 108.8 | C20—C21—H21B | 109.5 |
| C8—C9—H9A | 108.8 | H21A—C21—H21B | 109.5 |
| C1—C9—H9B | 108.8 | C20—C21—H21C | 109.5 |
| C8—C9—H9B | 108.8 | H21A—C21—H21C | 109.5 |
| H9A—C9—H9B | 107.7 | H21B—C21—H21C | 109.5 |
| C8—C10—H10A | 109.5 | | |
| | | | |
| C5—O1—C1—C2 | −9.1 (3) | C10—C8—C9—C1 | −76.1 (2) |
| C5—O1—C1—C9 | 169.84 (15) | C11—C8—C9—C1 | 163.06 (16) |
| O1—C1—C2—C6 | −177.43 (15) | C13—N2—C12—O3 | −178.32 (17) |
| C9—C1—C2—C6 | 3.8 (3) | C13—N2—C12—C3 | 2.29 (19) |
| O1—C1—C2—C3 | 3.2 (3) | C2—C3—C12—O3 | −61.1 (2) |
| C9—C1—C2—C3 | −175.58 (17) | C4—C3—C12—O3 | 59.5 (2) |
| C1—C2—C3—C4 | 7.4 (2) | C18—C3—C12—O3 | 178.58 (17) |
| C6—C2—C3—C4 | −171.98 (15) | C2—C3—C12—N2 | 118.30 (15) |
| C1—C2—C3—C18 | −118.89 (19) | C4—C3—C12—N2 | −121.10 (16) |
| C6—C2—C3—C18 | 61.7 (2) | C18—C3—C12—N2 | −2.03 (17) |
| C1—C2—C3—C12 | 129.65 (18) | C12—N2—C13—C14 | 176.80 (18) |
| C6—C2—C3—C12 | −49.7 (2) | C12—N2—C13—C18 | −1.6 (2) |
| C2—C3—C4—C5 | −13.0 (2) | C18—C13—C14—C15 | 1.0 (3) |
| C18—C3—C4—C5 | 114.60 (19) | N2—C13—C14—C15 | −177.16 (17) |
| C12—C3—C4—C5 | −133.18 (18) | C13—C14—C15—C16 | 0.6 (3) |
| C2—C3—C4—C19 | 170.14 (16) | C14—C15—C16—C17 | −1.3 (3) |
| C18—C3—C4—C19 | −62.2 (2) | C15—C16—C17—C18 | 0.5 (3) |
| C12—C3—C4—C19 | 50.0 (2) | C16—C17—C18—C13 | 1.1 (3) |
| C19—C4—C5—N1 | 4.7 (3) | C16—C17—C18—C3 | 176.77 (18) |
| C3—C4—C5—N1 | −172.18 (17) | C14—C13—C18—C17 | −1.8 (3) |
| C19—C4—C5—O1 | −174.29 (16) | N2—C13—C18—C17 | 176.64 (16) |
| C3—C4—C5—O1 | 8.8 (3) | C14—C13—C18—C3 | −178.38 (16) |
| C1—O1—C5—N1 | −176.23 (15) | N2—C13—C18—C3 | 0.1 (2) |
| C1—O1—C5—C4 | 2.9 (3) | C2—C3—C18—C17 | 69.0 (2) |
| C1—C2—C6—O2 | 173.11 (17) | C4—C3—C18—C17 | −55.8 (2) |
| C3—C2—C6—O2 | −7.5 (3) | C12—C3—C18—C17 | −174.93 (18) |
| C1—C2—C6—C7 | −9.4 (2) | C2—C3—C18—C13 | −114.90 (17) |
| C3—C2—C6—C7 | 170.05 (16) | C4—C3—C18—C13 | 120.22 (16) |
| O2—C6—C7—C8 | −147.85 (17) | C12—C3—C18—C13 | 1.13 (18) |
| C2—C6—C7—C8 | 34.6 (2) | C20—O5—C19—O4 | 7.4 (3) |
| C6—C7—C8—C9 | −50.6 (2) | C20—O5—C19—C4 | −171.23 (16) |
| C6—C7—C8—C10 | 69.8 (2) | C5—C4—C19—O4 | −4.3 (3) |
| C6—C7—C8—C11 | −169.86 (16) | C3—C4—C19—O4 | 172.61 (17) |

| C2—C1—C9—C8 | −23.1 (3) | C5—C4—C19—O5 | 174.22 (16) |
| O1—C1—C9—C8 | 158.03 (15) | C3—C4—C19—O5 | −8.8 (2) |
| C7—C8—C9—C1 | 44.1 (2) | C19—O5—C20—C21 | 154.05 (17) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
| --- | --- | --- | --- | --- |
| N1—H1*A*···O4 | 0.88 | 2.03 | 2.658 (2) | 128 |
| N1—H1*B*···O3[i] | 0.88 | 1.92 | 2.794 (2) | 175 |
| N2—H2···O2[ii] | 0.88 | 2.04 | 2.8435 (19) | 152 |
| C16—H16···O4[iii] | 0.95 | 2.54 | 3.448 (2) | 159 |

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