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# *N*-(Fluoren-9-ylmethoxycarbonyl)-L-isoleucine

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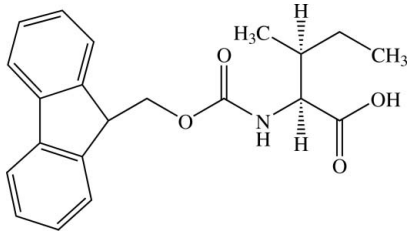
Key indicators: single-crystal X-ray study; $T$ = 90 K; mean $\sigma$(C–C) = 0.002 Å; $R$ factor = 0.035; $wR$ factor = 0.084; data-to-parameter ratio = 10.2.

In the crystal structure of the title compound [systematic name fluoren-9-ylmethyl *N*-(1-carboxy-2-methylbutyl)carbamate], $C_{21}H_{23}NO_4$, the molecular plane of the O=C—NH—$C_\alpha$ unit is slightly pyramidalized. The N atom deviates from the basal plane by 0.2086 (12) Å. The O=C—N—$C_\alpha$ torsion angle is −17.2 (2)°, and the C—N and O=C bond lengths are 1.3675 (17) and 1.2122 (17) Å, respectively. Apparently the character of the $sp^2$ hybrids of the molecular plane is, to some extent, reduced. The crystal structure exhibits two intermolecular hydrogen bonds (O—H···O and N—H···O), in which the hydroxy O atom acts as a donor to the carbonyl group and an acceptor of the amide group, respectively.

## Related literature

For related literature on the crystal structures of *N*-α-fluoren-9-ylmethoxycarbonyl-protected amino acids, see: Valle *et al.* (1984); Yamada, Hashizume & Shimizu (2008); Yamada, Hashizume, Shimizu *et al.* (2008).




## Experimental

### Crystal data

$C_{21}H_{23}NO_4$
$M_r$ = 353.40
Orthorhombic, $P2_12_12_1$
$a$ = 5.3337 (2) Å
$b$ = 13.6965 (4) Å
$c$ = 25.2514 (9) Å
$V$ = 1844.70 (11) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.09 mm$^{-1}$
$T$ = 90 K
0.77 × 0.06 × 0.04 mm

### Data collection

Rigaku AFC-8 diffractometer with Saturn70 CCD
Absorption correction: none
19825 measured reflections
3351 independent reflections
2993 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.043

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.084
$S$ = 1.03
3351 reflections
327 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.23 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1H···O2$^{i}$ | 0.88 (2) | 1.77 (2) | 2.6511 (14) | 176 (2) |
| N1—H1N···O1$^{ii}$ | 0.88 (2) | 2.18 (2) | 3.0433 (16) | 167.6 (17) |

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

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *HKL-2000* (Otwinowski & Minor, 1997); data reduction: *HKL-2000*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2313).

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# supporting information

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## *N*-(Fluoren-9-ylmethoxycarbonyl)-L-isoleucine

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### S1. Comment

The fluoren-9-ylmethoxycarbonyl (Fmoc) group is commonly used for protecting the terminal amine of the peptide for the current solid-phase peptide synthesis protocol. This is because cleavage of the Fmoc protecting group is easily achieved by mild basis conditions, *e.g*., piperidine, but it is very stable under acidic conditions. The crystal structures of *N*-*α*-Fmoc-protected-L-alanine monohydrate (Valle *et al.*, 1984), -*O*-*t*-butyl-L-serine (Yamada, Hashizume, Shimizu, Ohiki & Yokoyama, 2008) and –L-leucine (Yamada, Hashizume & Shimizu, 2008) have been studied. In this communication, we will report the structure of *N*-*α*-Fmoc-L-isoleucine, (I) (Fig. 1).

It is interesting to compare the present structure with that of the analog of the title compound, *i.e*., *N*-*α*-Fmoc-protected-L-leucine, (II). A large fraction of the bond distances and angles, and torsion angles of (I) are consistent with those of (II) except for the following points. First, the orientation of the carboxyl group around the C1—C6 bond is found to be opposite. The torsion angle of O2—C6—C1—N1 for (I) is -6.3 (2)°, while the corresponding angle of (II) is 159.29 (17)°. Second, the angle between the fluorine ring and the NC(=O)O plane is quite different. For example, the torsion angle of C7—O4—C8—C9 and O4—C8—C9—C10 are 121.17 (13) and -73.17 (14)°, respectively, for (I). The corresponding torsion angles of (II), on the other hand, are 93.78 (16) and 60.54 (17)°, respectively. Third, it can be seen that the O3—C7—N1—C1 plane of (I) is slightly pyramided. The N1 atom deviates from the basal plane (C1, C7, H1N) by 0.2086 (12) Å. Moreover, the distances of the N1—C7 and O3—C7 bonds are 1.3675 (17) and 1.2122 (17) Å, respectively, which are approximately 0.026 longer and 0.010 Å shorter than the corresponding bond lengths of (II), respectively. Apparently, the $sp^2$ character of the N1 atom is, to some extent, reduced.

In addition, hydrogen-bond environments are slightly different between the two Fmoc-protected L-amino acids. The crystal of (I) contains two intermolecular hydrogen bonds (Table 1), while that of (II) has three hydrogen bonds. For (I), atom O1 forms two hydrogen bonds with O2 and N1, as shown in Figure 2. The molecules, which related by translation along the *a* axis are assembled *via* the N1—H1N···O1 hydrogen bonds to form a one dimensional tape structure. The tapes around the $2_1$ axis, which is parallel to the *a* axis, are joined together, then the column structure is formed.

### S2. Experimental

A powdered sample of the title compound (I) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and was used for the sample preparation without further purifications. Colorless needle like crystals of (I) were obtained from a saturated dichloromethane solution.

### S3. Refinement

All H atoms were found on a difference map and were refined applying isotropic temperature factors.

The refined C—H, N—H or O—H dimensions are in the normal range: 0.975 (19)–1.015 (19) Å and 104.8 (10)–113.8 (11)° for C—H and C/N—C—H, respectively, for methyne; 0.942 (17)–1.01 (2) Å, 106.6 (13)–111.4 (12)° and

107.1 (18)–108.6 (14)° for C—H, C/O—C—H and H—C—H for methylene; 0.98 (3)–1.03 (3) Å, 109.5 (11)–112.8 (13)° and 104 (2)–111 (2)° for C—H, C—C—H and H—C—H, respectively, for methyl; 0.96 (2)–1.005 (19) Å and 117.7 (11)–123.1 (11)° for C—H and C—C—H, respectively, for aromatic; 0.88 (2) Å and 115.3 (12)–116.5 (12)° for N—H and C—N—H, respectively, for amide; 0.88 (2) Å and 108.7 (15)° for O—H and C—O—H, respectively, for hydroxyl. The range of the $U_{iso}$ values of the H atoms are 0.016 (4)–0.067 (8) Å$^2$.

In the absence of significant anomalous scattering effects, Friedel pairs have been merged.

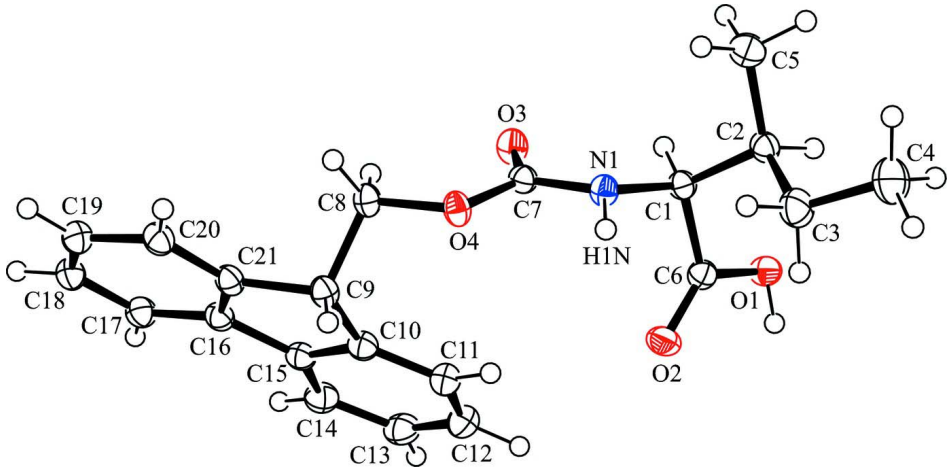


**Figure 1**

A view of the molecular structure of (I), showing the atom labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

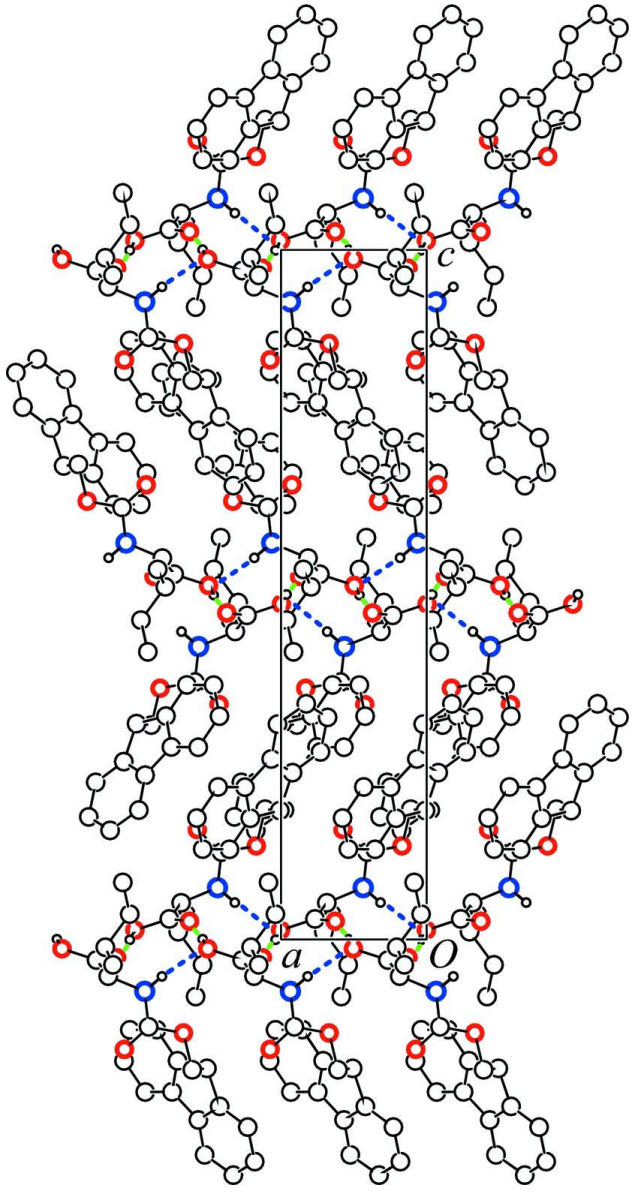


**Figure 2**

A packing diagram of (I). The hydrogen atoms were omitted for clarity, except for those forming the hydrogen bonds. The hydrogen bonds are shown as blue and green broken lines for N—H···O and O—H···O bonds, respectively.

### fluoren-9-ylmethyl N-(1-carboxy-2-methylbutyl)carbamate

*Crystal data*

$C_{21}H_{23}NO_4$
$M_r = 353.40$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 5.3337\ (2)$ Å
$b = 13.6965\ (4)$ Å
$c = 25.2514\ (9)$ Å
$V = 1844.70\ (11)$ Å$^3$
$Z = 4$
$F(000) = 752$
$D_x = 1.272$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 19896 reflections
$\theta = 1.6$–$31.0°$
$\mu = 0.09$ mm$^{-1}$
$T = 90$ K
Needle, colourless
0.77 × 0.06 × 0.04 mm

*Data collection*

Rigaku AFC-8 with Saturn70 CCD diffractometer
Radiation source: fine-focus rotating anode
Confocal monochromator
Detector resolution: 28.5714 pixels $mm^{-1}$
$\omega$ scans
19825 measured reflections
3351 independent reflections
2993 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 31.0°$, $\theta_{min} = 1.6°$
$h = -7 \rightarrow 7$
$k = -13 \rightarrow 19$
$l = -36 \rightarrow 36$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.084$
$S = 1.03$
3351 reflections
327 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.2178P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{min} = -0.18$ e Å$^{-3}$

*Special details*

**Experimental**. All Friedel pairs were merged, and all *f*''s of containing atoms were set to zero.

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > 2\sigma(F^2)$ 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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | −0.0029 (2) | 0.12876 (8) | 0.48657 (4) | 0.0236 (2) |
| H1H | −0.038 (4) | 0.1865 (16) | 0.5004 (8) | 0.040 (6)* |
| O2 | 0.3719 (2) | 0.19896 (8) | 0.47355 (4) | 0.0287 (2) |
| O3 | 0.4252 (2) | 0.06814 (8) | 0.34059 (4) | 0.0254 (2) |
| O4 | 0.83023 (19) | 0.09577 (8) | 0.36430 (4) | 0.0219 (2) |
| N1 | 0.5644 (2) | 0.03926 (9) | 0.42480 (4) | 0.0201 (2) |
| H1N | 0.683 (4) | 0.0588 (14) | 0.4465 (7) | 0.028 (5)* |
| C1 | 0.3145 (3) | 0.03122 (10) | 0.44681 (5) | 0.0198 (3) |
| H1 | 0.201 (4) | 0.0187 (13) | 0.4152 (7) | 0.029 (5)* |
| C2 | 0.2942 (3) | −0.05077 (10) | 0.48868 (5) | 0.0221 (3) |
| H2 | 0.124 (4) | −0.0497 (14) | 0.5026 (7) | 0.025 (5)* |
| C3 | 0.4615 (4) | −0.03098 (13) | 0.53677 (6) | 0.0322 (4) |
| H3A | 0.641 (5) | −0.0353 (16) | 0.5239 (9) | 0.045 (6)* |
| H3B | 0.433 (4) | 0.0382 (16) | 0.5491 (8) | 0.043 (6)* |
| C4 | 0.4141 (5) | −0.10079 (16) | 0.58280 (7) | 0.0429 (5) |
| H4A | 0.524 (5) | −0.0821 (19) | 0.6146 (10) | 0.063 (7)* |

| | | | | |
|---|---|---|---|---|
| H4B | 0.449 (5) | −0.1707 (17) | 0.5734 (9) | 0.050 (6)* |
| H4C | 0.237 (6) | −0.1000 (19) | 0.5925 (10) | 0.067 (8)* |
| C5 | 0.3466 (4) | −0.14964 (12) | 0.46325 (7) | 0.0321 (4) |
| H5A | 0.235 (4) | −0.1587 (15) | 0.4308 (9) | 0.043 (6)* |
| H5B | 0.302 (4) | −0.2030 (14) | 0.4887 (8) | 0.034 (5)* |
| H5C | 0.526 (5) | −0.1554 (16) | 0.4525 (8) | 0.040 (6)* |
| C6 | 0.2335 (3) | 0.12921 (10) | 0.47018 (5) | 0.0209 (3) |
| C7 | 0.5913 (3) | 0.06860 (10) | 0.37335 (5) | 0.0195 (3) |
| C8 | 0.8909 (3) | 0.12808 (11) | 0.31097 (5) | 0.0214 (3) |
| H8A | 1.018 (4) | 0.0822 (13) | 0.2966 (7) | 0.023 (4)* |
| H8B | 0.746 (3) | 0.1242 (12) | 0.2898 (6) | 0.016 (4)* |
| C9 | 0.9917 (3) | 0.23248 (10) | 0.31308 (5) | 0.0218 (3) |
| H9 | 1.136 (4) | 0.2340 (14) | 0.3393 (7) | 0.033 (5)* |
| C10 | 0.7894 (3) | 0.30772 (10) | 0.32413 (5) | 0.0227 (3) |
| C11 | 0.6461 (3) | 0.32177 (11) | 0.36923 (6) | 0.0273 (3) |
| H11 | 0.678 (4) | 0.2802 (14) | 0.4013 (7) | 0.032 (5)* |
| C12 | 0.4624 (3) | 0.39449 (12) | 0.36893 (6) | 0.0307 (3) |
| H12 | 0.365 (4) | 0.4056 (14) | 0.4011 (8) | 0.037 (5)* |
| C13 | 0.4225 (3) | 0.45181 (12) | 0.32390 (7) | 0.0307 (3) |
| H13 | 0.289 (4) | 0.5019 (16) | 0.3241 (8) | 0.038 (5)* |
| C14 | 0.5681 (3) | 0.43873 (11) | 0.27881 (6) | 0.0272 (3) |
| H14 | 0.540 (4) | 0.4779 (14) | 0.2461 (8) | 0.033 (5)* |
| C15 | 0.7524 (3) | 0.36682 (10) | 0.27912 (5) | 0.0222 (3) |
| C16 | 0.9326 (3) | 0.33767 (10) | 0.23824 (5) | 0.0218 (3) |
| C17 | 0.9758 (3) | 0.37521 (11) | 0.18767 (5) | 0.0251 (3) |
| H17 | 0.877 (4) | 0.4283 (15) | 0.1741 (7) | 0.033 (5)* |
| C18 | 1.1730 (3) | 0.33647 (11) | 0.15819 (6) | 0.0271 (3) |
| H18 | 1.201 (4) | 0.3628 (13) | 0.1225 (7) | 0.027 (4)* |
| C19 | 1.3197 (3) | 0.26081 (11) | 0.17784 (6) | 0.0270 (3) |
| H19 | 1.452 (4) | 0.2330 (14) | 0.1573 (7) | 0.030 (5)* |
| C20 | 1.2715 (3) | 0.22127 (11) | 0.22789 (6) | 0.0248 (3) |
| H20 | 1.374 (4) | 0.1663 (14) | 0.2398 (7) | 0.029 (5)* |
| C21 | 1.0792 (3) | 0.26106 (10) | 0.25795 (5) | 0.0219 (3) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0187 (5) | 0.0237 (5) | 0.0284 (5) | 0.0005 (4) | 0.0011 (4) | −0.0042 (4) |
| O2 | 0.0264 (6) | 0.0232 (5) | 0.0365 (5) | −0.0060 (5) | 0.0050 (5) | −0.0056 (4) |
| O3 | 0.0191 (5) | 0.0341 (5) | 0.0231 (4) | −0.0028 (5) | −0.0025 (4) | 0.0014 (4) |
| O4 | 0.0169 (5) | 0.0277 (5) | 0.0210 (4) | −0.0022 (4) | −0.0003 (4) | 0.0047 (4) |
| N1 | 0.0162 (5) | 0.0243 (5) | 0.0199 (5) | −0.0010 (5) | −0.0006 (4) | 0.0006 (4) |
| C1 | 0.0166 (6) | 0.0209 (6) | 0.0219 (6) | −0.0012 (5) | 0.0009 (5) | −0.0011 (5) |
| C2 | 0.0196 (6) | 0.0214 (6) | 0.0254 (6) | −0.0013 (5) | 0.0031 (5) | 0.0008 (5) |
| C3 | 0.0373 (10) | 0.0340 (8) | 0.0253 (7) | −0.0043 (7) | −0.0023 (6) | 0.0050 (6) |
| C4 | 0.0577 (13) | 0.0424 (10) | 0.0287 (8) | −0.0021 (10) | −0.0003 (8) | 0.0117 (7) |
| C5 | 0.0400 (10) | 0.0229 (7) | 0.0334 (7) | 0.0015 (7) | 0.0038 (7) | 0.0012 (6) |
| C6 | 0.0197 (7) | 0.0229 (6) | 0.0203 (5) | −0.0006 (6) | −0.0005 (5) | −0.0009 (5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C7 | 0.0177 (6) | 0.0186 (6) | 0.0222 (6) | −0.0001 (5) | 0.0011 (5) | −0.0005 (4) |
| C8 | 0.0203 (7) | 0.0250 (6) | 0.0189 (5) | −0.0008 (6) | 0.0003 (5) | 0.0040 (5) |
| C9 | 0.0197 (6) | 0.0244 (6) | 0.0214 (6) | −0.0024 (5) | −0.0004 (5) | 0.0024 (5) |
| C10 | 0.0221 (7) | 0.0228 (6) | 0.0233 (6) | −0.0024 (6) | −0.0008 (5) | −0.0009 (5) |
| C11 | 0.0298 (8) | 0.0280 (7) | 0.0239 (6) | −0.0033 (6) | 0.0026 (6) | −0.0008 (5) |
| C12 | 0.0306 (8) | 0.0310 (8) | 0.0306 (7) | −0.0015 (7) | 0.0065 (6) | −0.0053 (6) |
| C13 | 0.0287 (8) | 0.0268 (7) | 0.0367 (7) | 0.0032 (7) | 0.0011 (6) | −0.0055 (6) |
| C14 | 0.0292 (8) | 0.0239 (7) | 0.0287 (7) | 0.0014 (6) | −0.0022 (6) | −0.0001 (5) |
| C15 | 0.0217 (7) | 0.0215 (6) | 0.0234 (6) | −0.0035 (6) | −0.0012 (5) | −0.0013 (5) |
| C16 | 0.0206 (7) | 0.0215 (6) | 0.0234 (6) | −0.0034 (5) | −0.0004 (5) | −0.0001 (5) |
| C17 | 0.0295 (8) | 0.0228 (6) | 0.0230 (6) | −0.0015 (6) | −0.0005 (6) | 0.0018 (5) |
| C18 | 0.0322 (9) | 0.0267 (7) | 0.0224 (6) | −0.0064 (6) | 0.0031 (6) | 0.0012 (5) |
| C19 | 0.0245 (8) | 0.0290 (7) | 0.0274 (6) | −0.0037 (6) | 0.0040 (6) | −0.0027 (5) |
| C20 | 0.0209 (7) | 0.0257 (7) | 0.0277 (6) | −0.0028 (6) | 0.0008 (6) | 0.0007 (5) |
| C21 | 0.0192 (7) | 0.0233 (6) | 0.0230 (6) | −0.0039 (6) | −0.0005 (5) | 0.0012 (5) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O1—C6 | 1.3270 (18) | C8—H8B | 0.942 (17) |
| O1—H1H | 0.88 (2) | C9—C10 | 1.518 (2) |
| O2—C6 | 1.2102 (18) | C9—C21 | 1.5196 (18) |
| O3—C7 | 1.2122 (17) | C9—H9 | 1.01 (2) |
| O4—C7 | 1.3471 (17) | C10—C11 | 1.385 (2) |
| O4—C8 | 1.4541 (16) | C10—C15 | 1.4092 (19) |
| N1—C7 | 1.3675 (17) | C11—C12 | 1.397 (2) |
| N1—C1 | 1.4484 (18) | C11—H11 | 1.005 (19) |
| N1—H1N | 0.88 (2) | C12—C13 | 1.398 (2) |
| C1—C6 | 1.5284 (19) | C12—H12 | 0.98 (2) |
| C1—C2 | 1.5462 (19) | C13—C14 | 1.390 (2) |
| C1—H1 | 1.015 (19) | C13—H13 | 0.99 (2) |
| C2—C5 | 1.525 (2) | C14—C15 | 1.392 (2) |
| C2—C3 | 1.531 (2) | C14—H14 | 1.00 (2) |
| C2—H2 | 0.975 (19) | C15—C16 | 1.466 (2) |
| C3—C4 | 1.526 (2) | C16—C17 | 1.3957 (19) |
| C3—H3A | 1.01 (2) | C16—C21 | 1.400 (2) |
| C3—H3B | 1.01 (2) | C17—C18 | 1.393 (2) |
| C4—H4A | 1.03 (3) | C17—H17 | 0.96 (2) |
| C4—H4B | 1.00 (2) | C18—C19 | 1.390 (2) |
| C4—H4C | 0.98 (3) | C18—H18 | 0.983 (18) |
| C5—H5A | 1.02 (2) | C19—C20 | 1.399 (2) |
| C5—H5B | 1.00 (2) | C19—H19 | 0.96 (2) |
| C5—H5C | 1.00 (2) | C20—C21 | 1.387 (2) |
| C8—C9 | 1.529 (2) | C20—H20 | 0.98 (2) |
| C8—H8A | 0.993 (19) | | |
| | | | |
| C6—O1—H1H | 108.7 (15) | C9—C8—H8B | 111.2 (10) |
| C7—O4—C8 | 116.86 (11) | H8A—C8—H8B | 108.6 (14) |
| C7—N1—C1 | 118.91 (12) | C10—C9—C21 | 102.23 (11) |

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|---|---|---|---|
| C7—N1—H1N | 115.3 (12) | C10—C9—C8 | 113.04 (12) |
| C1—N1—H1N | 116.5 (12) | C21—C9—C8 | 108.49 (11) |
| N1—C1—C6 | 109.97 (11) | C10—C9—H9 | 113.8 (11) |
| N1—C1—C2 | 112.46 (11) | C21—C9—H9 | 111.1 (11) |
| C6—C1—C2 | 110.73 (11) | C8—C9—H9 | 108.0 (11) |
| N1—C1—H1 | 105.0 (11) | C11—C10—C15 | 120.39 (14) |
| C6—C1—H1 | 106.5 (10) | C11—C10—C9 | 129.63 (13) |
| C2—C1—H1 | 111.9 (11) | C15—C10—C9 | 109.96 (12) |
| C5—C2—C3 | 112.62 (14) | C10—C11—C12 | 118.80 (14) |
| C5—C2—C1 | 110.13 (12) | C10—C11—H11 | 119.3 (11) |
| C3—C2—C1 | 111.90 (12) | C12—C11—H11 | 121.9 (11) |
| C5—C2—H2 | 109.7 (11) | C11—C12—C13 | 120.76 (15) |
| C3—C2—H2 | 104.8 (10) | C11—C12—H12 | 118.6 (12) |
| C1—C2—H2 | 107.5 (11) | C13—C12—H12 | 120.6 (12) |
| C4—C3—C2 | 113.36 (15) | C14—C13—C12 | 120.59 (15) |
| C4—C3—H3A | 111.4 (12) | C14—C13—H13 | 119.7 (12) |
| C2—C3—H3A | 106.6 (13) | C12—C13—H13 | 119.7 (12) |
| C4—C3—H3B | 109.2 (12) | C13—C14—C15 | 118.76 (14) |
| C2—C3—H3B | 108.9 (12) | C13—C14—H14 | 121.6 (12) |
| H3A—C3—H3B | 107.1 (19) | C15—C14—H14 | 119.6 (12) |
| C3—C4—H4A | 110.2 (15) | C14—C15—C10 | 120.68 (13) |
| C3—C4—H4B | 112.8 (13) | C14—C15—C16 | 130.69 (13) |
| H4A—C4—H4B | 109 (2) | C10—C15—C16 | 108.64 (13) |
| C3—C4—H4C | 110.1 (16) | C17—C16—C21 | 120.60 (13) |
| H4A—C4—H4C | 111 (2) | C17—C16—C15 | 130.71 (14) |
| H4B—C4—H4C | 104 (2) | C21—C16—C15 | 108.66 (12) |
| C2—C5—H5A | 109.8 (12) | C18—C17—C16 | 118.24 (14) |
| C2—C5—H5B | 109.5 (11) | C18—C17—H17 | 120.8 (12) |
| H5A—C5—H5B | 106.7 (17) | C16—C17—H17 | 121.0 (12) |
| C2—C5—H5C | 111.2 (13) | C19—C18—C17 | 121.20 (14) |
| H5A—C5—H5C | 109.4 (17) | C19—C18—H18 | 121.0 (11) |
| H5B—C5—H5C | 110.2 (17) | C17—C18—H18 | 117.7 (11) |
| O2—C6—O1 | 124.13 (13) | C18—C19—C20 | 120.52 (15) |
| O2—C6—C1 | 123.22 (13) | C18—C19—H19 | 121.3 (11) |
| O1—C6—C1 | 112.64 (12) | C20—C19—H19 | 118.1 (11) |
| O3—C7—O4 | 125.25 (12) | C21—C20—C19 | 118.54 (14) |
| O3—C7—N1 | 124.76 (13) | C21—C20—H20 | 123.1 (11) |
| O4—C7—N1 | 109.97 (12) | C19—C20—H20 | 118.4 (11) |
| O4—C8—C9 | 109.32 (11) | C20—C21—C16 | 120.86 (12) |
| O4—C8—H8A | 107.3 (10) | C20—C21—C9 | 128.82 (13) |
| C9—C8—H8A | 111.3 (10) | C16—C21—C9 | 110.31 (12) |
| O4—C8—H8B | 109.0 (10) | | |

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|---|---|---|---|
| C7—N1—C1—C6 | −88.14 (15) | C12—C13—C14—C15 | 0.7 (2) |
| C7—N1—C1—C2 | 147.96 (12) | C13—C14—C15—C10 | 0.6 (2) |
| N1—C1—C2—C5 | −62.96 (16) | C13—C14—C15—C16 | −179.33 (15) |
| C6—C1—C2—C5 | 173.56 (13) | C11—C10—C15—C14 | −1.4 (2) |
| N1—C1—C2—C3 | 63.11 (16) | C9—C10—C15—C14 | 177.23 (13) |

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| C6—C1—C2—C3 | −60.37 (16) | C11—C10—C15—C16 | 178.54 (13) |
| C5—C2—C3—C4 | −65.0 (2) | C9—C10—C15—C16 | −2.87 (16) |
| C1—C2—C3—C4 | 170.27 (15) | C14—C15—C16—C17 | 1.9 (3) |
| N1—C1—C6—O2 | −6.34 (19) | C10—C15—C16—C17 | −178.03 (15) |
| C2—C1—C6—O2 | 118.56 (15) | C14—C15—C16—C21 | 179.97 (15) |
| N1—C1—C6—O1 | 174.17 (11) | C10—C15—C16—C21 | 0.08 (16) |
| C2—C1—C6—O1 | −60.94 (15) | C21—C16—C17—C18 | −1.9 (2) |
| C8—O4—C7—O3 | 0.8 (2) | C15—C16—C17—C18 | 176.00 (14) |
| C8—O4—C7—N1 | 179.33 (11) | C16—C17—C18—C19 | 1.5 (2) |
| C1—N1—C7—O3 | −17.2 (2) | C17—C18—C19—C20 | 0.3 (2) |
| C1—N1—C7—O4 | 164.18 (11) | C18—C19—C20—C21 | −1.8 (2) |
| C7—O4—C8—C9 | 121.17 (13) | C19—C20—C21—C16 | 1.4 (2) |
| O4—C8—C9—C10 | −73.17 (14) | C19—C20—C21—C9 | −179.33 (14) |
| O4—C8—C9—C21 | 174.19 (12) | C17—C16—C21—C20 | 0.5 (2) |
| C21—C9—C10—C11 | −177.33 (15) | C15—C16—C21—C20 | −177.88 (13) |
| C8—C9—C10—C11 | 66.3 (2) | C17—C16—C21—C9 | −178.93 (13) |
| C21—C9—C10—C15 | 4.25 (15) | C15—C16—C21—C9 | 2.74 (16) |
| C8—C9—C10—C15 | −112.17 (13) | C10—C9—C21—C20 | 176.47 (14) |
| C15—C10—C11—C12 | 0.9 (2) | C8—C9—C21—C20 | −63.88 (19) |
| C9—C10—C11—C12 | −177.41 (15) | C10—C9—C21—C16 | −4.22 (15) |
| C10—C11—C12—C13 | 0.4 (2) | C8—C9—C21—C16 | 115.44 (13) |
| C11—C12—C13—C14 | −1.2 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*H*···O2$^{i}$ | 0.88 (2) | 1.77 (2) | 2.6511 (14) | 176 (2) |
| N1—H1*N*···O1$^{ii}$ | 0.88 (2) | 2.18 (2) | 3.0433 (16) | 167.6 (17) |

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