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# Synthesis and structure of photodegradable 1-(4,5-dimethoxy-2,3-dinitrophenyl)-2-methylpropyl *N*-butylcarbamate

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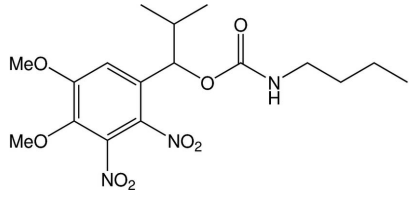
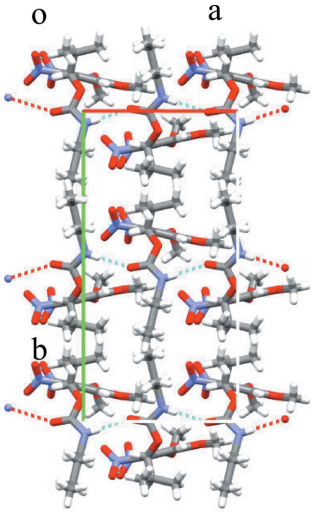
The reaction of 1-(4,5-dimethoxy-2,3-dinitrophenyl)-2-methylpropan-1-ol and butylisocyanate using dibutyltin dilaurate as a catalyst afforded 1-(4,5-dimethoxy-2,3-dinitrophenyl)-2-methylpropyl *N*-butylcarbamate, $C_{17}H_{25}N_3O_8$, which released butylamine upon photoirradiation. Single crystals of the title compound were grown in a 1:1 mixed solution of hexane and ethyl acetate. Two nitro groups and one methoxy group are twisted out of the plane of the aromatic ring in the novel photo-protecting group. Intermolecular hydrogen bonds are observed between *N*-butylcarbamate moieties parallel to the *a* axis.

## 1. Chemical context

Photodegradable protective groups (PPGs) are common tools in the field of organic, biochemical, and materials sciences (Cambie *et al.*, 2016; Ellis-Davies, 2020; Hansen *et al.*, 2015). 2-Nitrobenzyl groups are widely used as PPGs because several precursors are available, they react with various functional groups and the resulting protected compounds are soluble in common organic solvents. To increase the sensitivity of 2-nitrobenzyl-group-protected derivatives, several chemical modifications, such as the introduction of substituents at the $\alpha$-position, have been performed (Kasuga *et al.*, 2016; Zhao *et al.*, 2012).




Herein, we report the synthesis and structure of the novel photolabile title compound 1-(4,5-dimethoxy-2,3-dinitrophenyl)-2-methylpropyl *N*-butylcarbamate (**1**), which has an isopropyl group at the $\alpha$-position and an additional nitro group at the 3-position. It was prepared from the corresponding alcohol and isocyanate using a tin catalyst based on a previously reported reaction with modifications (Stegmaier *et al.*, 2008) and the amine was released upon photoirradiation, which indicated that the compound has high reactivity and the potential for application in various functional materials. Compound **1** exhibits a higher sensitivity to light than the corresponding compound with one nitro group at the *ortho* position (Kasuga *et al.*, 2015).

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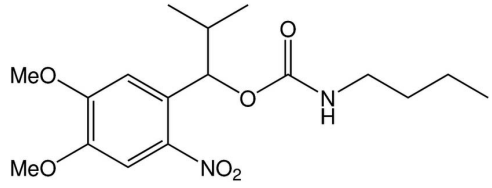
## 2. Structural commentary

The asymmetric unit of **1** contains a single molecule in which four functional groups and a carbamate linkage site are connected to the aromatic ring. The substituents are positioned in a manner that prevents steric repulsion (Fig. 1).

The aromatic ring (C1–C6) and five attached atoms (N1, N2, O5, O6, and C7) are almost planar, as indicated by the torsion angles N2—C3—C2—N1 = 4.4 (3)°, O5—C4—C5—O6 = −8.0 (3)°, and C7—C1—C2—N1 = −4.3 (3)°. However, the torsion angles involving the two nitro groups [O2—N1—C2—C1 = 56.9 (3)°, O1—N1—C2—C1 = −122.5 (2)°, O3—N2—C3—C2 = −125.9 (3)°, and O4—N2—C3—C2 = 53.9 (3)°] indicate that both $NO_2$ groups are twisted relative to the plane of the aromatic ring. The torsion angles involving the two methoxy groups [C16—O5—C4—C3 and C17—O6—C5—C4) are −110.7 (2)° and 172.5 (2)°] indicate that one methoxy group (O5–C16) is twisted and the other (O6–C17) is located in the same plane as the aromatic ring.

In the related compound, 4,5-dimethoxy-2-nitrobenzyl acetate (shown in the scheme below), the nitro and dimethoxy groups are in the same plane as the aromatic ring and the whole molecule is flat in the absence of substituents at the $\alpha$-position (Kasuga *et al.*, 2015).




## 3. Supramolecular features

In the crystal, N3—H3···O8$^{i}$ hydrogen bonds link the molecules into chains parallel to the *a* axis (Fig. 2 and Table 1).

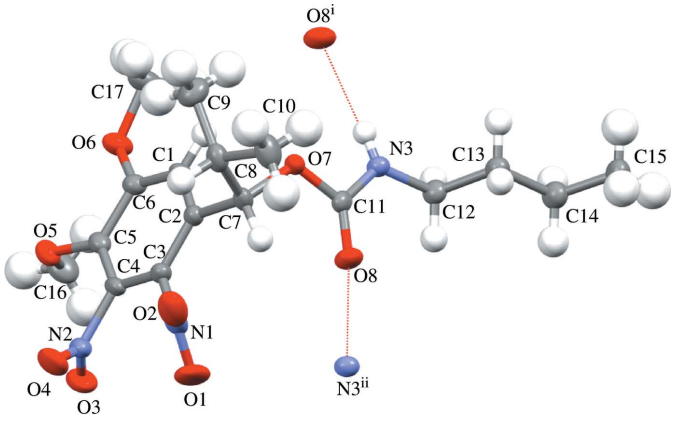



**Figure 1**
Molecular structure of photocleavable 1-(4,5-dimethoxy-2,3-dinitrophenyl)-2-methylpropyl butylcarbamate. Displacement ellipsoids are drawn at the 50% probability level. The intermolecular hydrogen bonds (Table 1) are drawn as dotted lines.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···O8$^{i}$ | 0.78 (3) | 2.26 (3) | 3.042 (3) | 176 (3) |

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

## 4. Synthesis and crystallization

The synthesis of compound **1** was based on the method reported by Stegmaier *et al.* (2008) with modifications. The synthesis and photocleavage is shown in the scheme below. This dinitrobenzyl protecting group photocleaved twice as fast as the corresponding 2-mononitrobenzyl group. Under an $N_2$ atmosphere, a mixture of 1-(4,5-dimethoxy-2,3-dinitrophenyl)-2-methylpropan-1-ol (150 mg, 0.5 mmol), *n*-butyl isocyanate (85 µ*L*, 0.75 mmol), dibutyltin laurate (15 µ*L*), and 1.5 ml of tetrahydrofuran were refluxed for 19 h. After

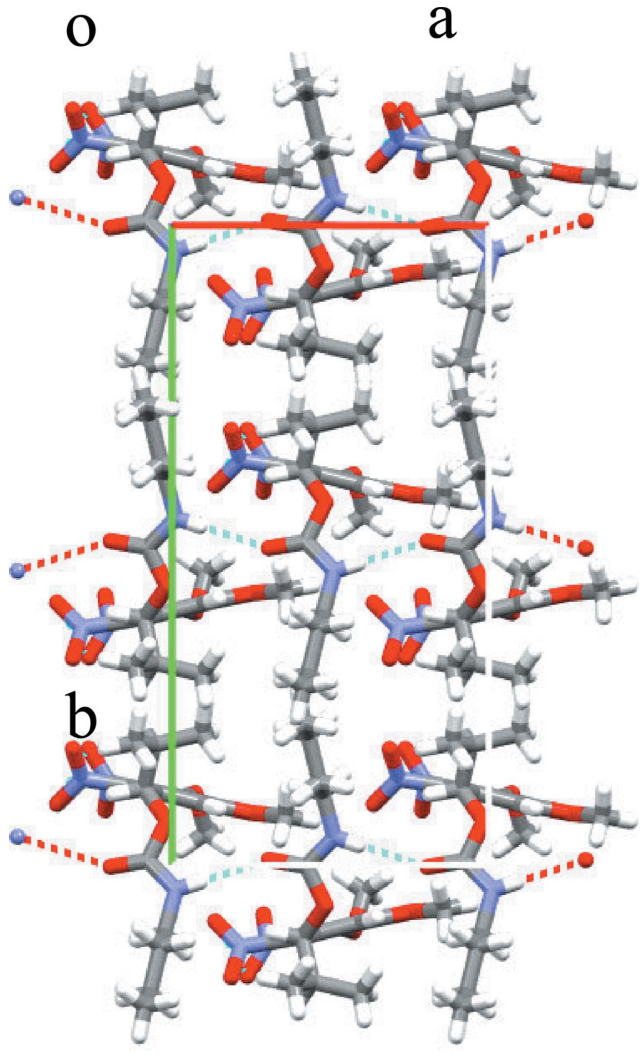
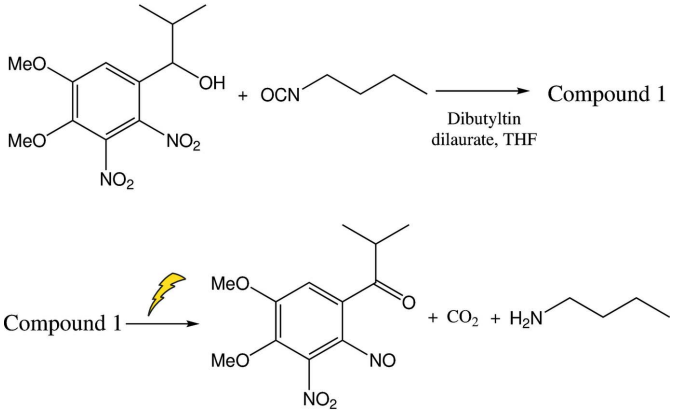



**Figure 2**
Intermolecular hydrogen bonds (Table 1) between the carbamate moieties, shown as dotted lines, link the molecules into chains parallel to the *a* axis.

removing the solvent, the crude solid was purified by silica gel column chromatography. Pale-yellow needle-shaped crystals were grown in a 1:1 mixed solution of hexane and ethyl acetate by slow evaporation. The crystals were washed with a small volume of ethyl acetate and dried *in vacuo* (50 mg).




Analysis calculated for $C_{17}H_{25}N_3O_8$: C 51.12, H 6.31, N 10.52%. Found: C 51.07, H 6.20, N 10.42%. Prominent IR bands at 1800–400 $cm^{-1}$ (KBr disc): 1693*m*, 1557*m*, 1359*m*. Melting point 379.9–381.1 K (uncorrected). $^1$H NMR ($CDCl_3$, 292.2 K) 0.90 (3H, *t*), 0.91 (3H, *d*), 1.03 (3H, *d*), 1.32 (2H, *m*), 1.45 (2H, *m*), 2.18 (1H, *m*), 3.13 (2H, *m*), 3.93 (6H, *s*), 4.76 (1H, *br*), 5.61 (1H, *d*), 6.97 (1H, *s*). $^{13}$C NMR ($CDCl_3$, 293.7 K) 13.69, 17.88, 19.21, 19.86, 31.88, 33.39, 40.85, 56.71, 62.58, 76.04, 111.29, 131.17, 134.82, 140.45, 141.14, 155.28, 155.84.

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The C-bound H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and refined using a riding model with $U_{iso}$(H) = 1.2 or 1.5$U_{eq}$(C).

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{17}H_{25}N_3O_8$ |
| $M_r$ | 399.40 |
| Crystal system, space group | Monoclinic, *Ia* |
| Temperature (K) | 120 |
| *a*, *b*, *c* (Å) | 9.9490 (4), 19.9223 (8), 10.2378 (4) |
| $\beta$ (°) | 97.616 (4) |
| $V$ (Å$^3$) | 2011.30 (14) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ ($mm^{-1}$) | 0.11 |
| Crystal size (mm) | 0.25 × 0.21 × 0.18 |
| Data collection | |
| Diffractometer | Rigaku VariMax SaturnCCD724 |
| Absorption correction | Multi-scan (*CrysAlis PRO*; Rigaku OD, 2018) |
| $T_{min}$, $T_{max}$ | 0.906, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 18806, 5927, 4720 |
| $R_{int}$ | 0.039 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.730 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.045, 0.094, 1.04 |
| No. of reflections | 5927 |
| No. of parameters | 262 |
| No. of restraints | 2 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.18, −0.19 |

Computer programs: *CrysAlis PRO* (Rigaku OD, 2018), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

## Acknowledgements

The support of Kanagawa University, including the use of the diffractometer, is gratefully acknowledged. Author contributions: conceptualization, MI, NCK, and KY; synthesis and analysis, HT, MI, and NCK; writing, NCK and KY; validation, NCK and HS.

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# supporting information

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## Synthesis and structure of photodegradable 1-(4,5-dimethoxy-2,3-dinitrophenyl)-2-methylpropyl *N*-butylcarbamate

**Takafumi Honda, Michiko Ito, Kazuo Yamaguchi, Noriko Chikaraishi Kasuga and Hiroyasu Sato**

### Computing details

Data collection: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.39.46 (Rigaku OD, 2018); program(s) used to solve structure: ShelXT (Sheldrick, 2015aa); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: Olex2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 (Dolomanov *et al.*, 2009).

### 1-(4,5-Dimethoxy-2,3-dinitrophenyl)-2-methylpropyl *N*-butylcarbamate

*Crystal data*

$C_{17}H_{25}N_3O_8$
$M_r$ = 399.40
Monoclinic, *Ia*
*a* = 9.9490 (4) Å
*b* = 19.9223 (8) Å
*c* = 10.2378 (4) Å
*β* = 97.616 (4)°
*V* = 2011.30 (14) Å$^3$
*Z* = 4
*F*(000) = 848
$D_x$ = 1.319 Mg m$^{-3}$
Melting point = 380.1–274.2 K
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 10281 reflections
*θ* = 3.4–31.2°
*μ* = 0.11 mm$^{-1}$
*T* = 120 K
Block, clear light yellow
0.25 × 0.21 × 0.18 mm

*Data collection*

Rigaku VariMax SaturnCCD724 diffractometer
Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source
Graphite monochromator
*ω* scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2018)
$T_{min}$ = 0.906, $T_{max}$ = 1.000
18806 measured reflections
5927 independent reflections
4720 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.039
$\theta_{max}$ = 31.3°, $\theta_{min}$ = 3.4°
*h* = −14→14
*k* = −27→28
*l* = −14→14

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.094
*S* = 1.03
5927 reflections
262 parameters
2 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.1525P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.18$ e Å$^{-3}$
$\Delta\rho_{min} = -0.18$ 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.

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

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.13662 (19) | 0.40830 (14) | 0.6373 (2) | 0.0649 (7) |
| O2 | 0.18717 (19) | 0.32139 (11) | 0.5256 (2) | 0.0512 (5) |
| O3 | 0.2890 (2) | 0.41867 (10) | 0.9547 (2) | 0.0502 (5) |
| O4 | 0.2377 (2) | 0.32211 (10) | 0.8644 (2) | 0.0483 (5) |
| O5 | 0.57340 (17) | 0.39172 (8) | 0.96576 (16) | 0.0313 (4) |
| O6 | 0.75485 (16) | 0.42284 (9) | 0.80062 (16) | 0.0341 (4) |
| O7 | 0.48515 (15) | 0.43395 (7) | 0.34698 (15) | 0.0246 (3) |
| O8 | 0.30610 (16) | 0.50552 (8) | 0.34710 (17) | 0.0349 (4) |
| N1 | 0.2168 (2) | 0.36864 (14) | 0.5995 (2) | 0.0403 (6) |
| N2 | 0.3014 (2) | 0.37462 (11) | 0.8748 (2) | 0.0346 (5) |
| N3 | 0.5126 (2) | 0.54139 (9) | 0.30272 (19) | 0.0248 (4) |
| C1 | 0.4522 (2) | 0.38928 (11) | 0.5581 (2) | 0.0242 (5) |
| C2 | 0.3608 (2) | 0.38015 (11) | 0.6472 (2) | 0.0266 (5) |
| C3 | 0.4010 (2) | 0.38545 (11) | 0.7824 (2) | 0.0270 (5) |
| C4 | 0.5334 (2) | 0.39790 (11) | 0.8338 (2) | 0.0260 (5) |
| C5 | 0.6271 (2) | 0.40978 (11) | 0.7437 (2) | 0.0255 (5) |
| C6 | 0.5857 (2) | 0.40607 (11) | 0.6096 (2) | 0.0249 (5) |
| C7 | 0.4121 (2) | 0.38328 (11) | 0.4104 (2) | 0.0262 (5) |
| C8 | 0.4431 (3) | 0.31488 (12) | 0.3535 (2) | 0.0309 (5) |
| C9 | 0.5937 (3) | 0.29733 (13) | 0.3712 (3) | 0.0413 (6) |
| C10 | 0.3836 (3) | 0.31118 (14) | 0.2093 (3) | 0.0426 (7) |
| C11 | 0.4244 (2) | 0.49560 (11) | 0.3336 (2) | 0.0233 (4) |
| C12 | 0.4751 (2) | 0.61096 (11) | 0.2740 (2) | 0.0288 (5) |
| C13 | 0.4652 (2) | 0.62909 (11) | 0.1295 (2) | 0.0289 (5) |
| C14 | 0.4296 (3) | 0.70286 (12) | 0.1055 (3) | 0.0374 (6) |
| C15 | 0.4166 (3) | 0.72204 (14) | −0.0381 (3) | 0.0421 (7) |
| C16 | 0.6073 (3) | 0.45403 (14) | 1.0351 (3) | 0.0446 (7) |
| C17 | 0.8593 (2) | 0.42724 (15) | 0.7164 (3) | 0.0412 (7) |
| H3 | 0.588 (3) | 0.5291 (12) | 0.310 (3) | 0.026 (7)* |
| H6 | 0.648082 | 0.414974 | 0.551752 | 0.030* |
| H7 | 0.314682 | 0.392050 | 0.389922 | 0.031* |
| H8 | 0.397129 | 0.280852 | 0.400680 | 0.037* |
| H9A | 0.642527 | 0.331190 | 0.330187 | 0.062* |
| H9B | 0.606179 | 0.254638 | 0.331034 | 0.062* |
| H9C | 0.627043 | 0.295128 | 0.463472 | 0.062* |
| H10A | 0.288238 | 0.320714 | 0.200686 | 0.064* |

| | | | | |
|---|---|---|---|---|
| H10B | 0.397234 | 0.266968 | 0.176167 | 0.064* |
| H10C | 0.427650 | 0.343506 | 0.159920 | 0.064* |
| H12A | 0.541687 | 0.639913 | 0.323654 | 0.035* |
| H12B | 0.388247 | 0.619657 | 0.303969 | 0.035* |
| H13A | 0.396452 | 0.601434 | 0.079559 | 0.035* |
| H13B | 0.551210 | 0.619674 | 0.098363 | 0.035* |
| H14A | 0.344649 | 0.712310 | 0.138677 | 0.045* |
| H14B | 0.499305 | 0.730341 | 0.154638 | 0.045* |
| H15A | 0.500225 | 0.712690 | −0.071672 | 0.063* |
| H15B | 0.396447 | 0.769065 | −0.047350 | 0.063* |
| H15C | 0.344706 | 0.696579 | −0.086689 | 0.063* |
| H16A | 0.675426 | 0.477282 | 0.994558 | 0.067* |
| H16B | 0.641171 | 0.444566 | 1.125445 | 0.067* |
| H16C | 0.527663 | 0.481566 | 1.031391 | 0.067* |
| H17A | 0.839687 | 0.463759 | 0.655666 | 0.062* |
| H17B | 0.862726 | 0.386057 | 0.668233 | 0.062* |
| H17C | 0.945213 | 0.434835 | 0.768997 | 0.062* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0257 (10) | 0.1028 (19) | 0.0698 (16) | 0.0228 (11) | 0.0194 (10) | 0.0230 (14) |
| O2 | 0.0328 (10) | 0.0666 (14) | 0.0513 (13) | −0.0210 (10) | −0.0052 (9) | 0.0176 (11) |
| O3 | 0.0577 (13) | 0.0498 (12) | 0.0502 (13) | 0.0163 (10) | 0.0334 (10) | 0.0051 (9) |
| O4 | 0.0390 (11) | 0.0518 (13) | 0.0586 (14) | −0.0083 (9) | 0.0227 (9) | 0.0144 (10) |
| O5 | 0.0398 (10) | 0.0322 (9) | 0.0233 (8) | −0.0001 (7) | 0.0097 (7) | −0.0013 (7) |
| O6 | 0.0253 (8) | 0.0503 (11) | 0.0274 (9) | −0.0058 (7) | 0.0067 (7) | −0.0059 (7) |
| O7 | 0.0201 (7) | 0.0261 (8) | 0.0288 (8) | 0.0013 (6) | 0.0069 (6) | 0.0082 (6) |
| O8 | 0.0193 (8) | 0.0366 (9) | 0.0498 (11) | 0.0031 (7) | 0.0078 (7) | 0.0056 (8) |
| N1 | 0.0195 (10) | 0.0607 (15) | 0.0417 (13) | 0.0005 (10) | 0.0079 (9) | 0.0249 (11) |
| N2 | 0.0297 (11) | 0.0389 (12) | 0.0384 (12) | 0.0114 (10) | 0.0170 (9) | 0.0152 (10) |
| N3 | 0.0199 (9) | 0.0250 (10) | 0.0301 (10) | 0.0015 (8) | 0.0051 (8) | 0.0023 (7) |
| C1 | 0.0215 (11) | 0.0249 (11) | 0.0269 (12) | 0.0025 (8) | 0.0059 (9) | 0.0063 (9) |
| C2 | 0.0197 (10) | 0.0296 (12) | 0.0316 (13) | 0.0027 (9) | 0.0073 (9) | 0.0087 (9) |
| C3 | 0.0256 (11) | 0.0253 (11) | 0.0333 (12) | 0.0052 (9) | 0.0157 (9) | 0.0087 (9) |
| C4 | 0.0298 (12) | 0.0239 (11) | 0.0259 (12) | 0.0032 (9) | 0.0105 (9) | 0.0008 (8) |
| C5 | 0.0234 (11) | 0.0259 (11) | 0.0280 (12) | 0.0006 (9) | 0.0067 (9) | −0.0016 (9) |
| C6 | 0.0208 (10) | 0.0283 (12) | 0.0278 (12) | −0.0005 (9) | 0.0114 (9) | 0.0032 (9) |
| C7 | 0.0206 (10) | 0.0303 (12) | 0.0278 (12) | −0.0034 (9) | 0.0034 (9) | 0.0104 (9) |
| C8 | 0.0343 (13) | 0.0287 (12) | 0.0293 (12) | −0.0065 (10) | 0.0021 (10) | 0.0062 (9) |
| C9 | 0.0410 (15) | 0.0332 (14) | 0.0485 (17) | 0.0066 (12) | 0.0019 (12) | −0.0069 (12) |
| C10 | 0.0525 (16) | 0.0427 (15) | 0.0310 (14) | −0.0119 (13) | −0.0006 (12) | 0.0028 (11) |
| C11 | 0.0228 (11) | 0.0278 (11) | 0.0189 (10) | 0.0037 (9) | 0.0008 (8) | 0.0024 (8) |
| C12 | 0.0302 (12) | 0.0232 (11) | 0.0332 (13) | 0.0023 (9) | 0.0050 (10) | 0.0002 (9) |
| C13 | 0.0252 (11) | 0.0268 (12) | 0.0351 (13) | 0.0001 (9) | 0.0052 (9) | 0.0028 (10) |
| C14 | 0.0370 (14) | 0.0301 (13) | 0.0459 (16) | 0.0013 (11) | 0.0087 (12) | 0.0065 (11) |
| C15 | 0.0353 (14) | 0.0404 (16) | 0.0510 (17) | 0.0019 (12) | 0.0071 (12) | 0.0169 (13) |
| C16 | 0.0603 (19) | 0.0421 (16) | 0.0335 (15) | −0.0066 (13) | 0.0147 (13) | −0.0108 (11) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C17 | 0.0259 (13) | 0.0651 (19) | 0.0339 (15) | −0.0097 (12) | 0.0085 (11) | −0.0077 (13) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O2—N1 | 1.219 (3) | C8—C9 | 1.525 (4) |
| O3—N2 | 1.217 (3) | C8—C10 | 1.518 (4) |
| O5—C4 | 1.363 (3) | C9—H9A | 0.9600 |
| O5—C16 | 1.448 (3) | C9—H9B | 0.9600 |
| O8—C11 | 1.220 (3) | C9—H9C | 0.9600 |
| O6—C5 | 1.351 (3) | C10—H10A | 0.9600 |
| O6—C17 | 1.438 (3) | C10—H10B | 0.9600 |
| O7—C11 | 1.367 (3) | C10—H10C | 0.9600 |
| O7—C7 | 1.447 (2) | C12—H12A | 0.9700 |
| N1—O1 | 1.222 (3) | C12—H12B | 0.9700 |
| N1—C2 | 1.469 (3) | C12—C13 | 1.513 (3) |
| N2—O4 | 1.220 (3) | C13—H13A | 0.9700 |
| N2—C3 | 1.473 (3) | C13—H13B | 0.9700 |
| N3—C11 | 1.332 (3) | C13—C14 | 1.524 (3) |
| N3—C12 | 1.455 (3) | C14—H14A | 0.9700 |
| N3—H3 | 0.78 (3) | C14—H14B | 0.9700 |
| C1—C6 | 1.402 (3) | C14—C15 | 1.508 (4) |
| C1—C2 | 1.383 (3) | C15—H15A | 0.9600 |
| C1—C7 | 1.517 (3) | C15—H15B | 0.9600 |
| C3—C2 | 1.394 (3) | C15—H15C | 0.9600 |
| C4—C3 | 1.374 (3) | C16—H16A | 0.9600 |
| C4—C5 | 1.416 (3) | C16—H16B | 0.9600 |
| C6—H6 | 0.9300 | C16—H16C | 0.9600 |
| C6—C5 | 1.382 (3) | C17—H17A | 0.9600 |
| C7—H7 | 0.9800 | C17—H17B | 0.9600 |
| C8—H8 | 0.9800 | C17—H17C | 0.9600 |
| C8—C7 | 1.529 (3) | | |

| | | | |
|---|---|---|---|
| O1—N1—C2 | 116.3 (3) | C8—C9—H9C | 109.5 |
| O2—N1—O1 | 125.6 (2) | C8—C10—H10A | 109.5 |
| O2—N1—C2 | 118.1 (2) | C8—C10—H10B | 109.5 |
| O3—N2—O4 | 125.4 (2) | C8—C10—H10C | 109.5 |
| O3—N2—C3 | 117.5 (2) | C9—C8—H8 | 107.3 |
| O4—N2—C3 | 117.1 (2) | C9—C8—C7 | 113.8 (2) |
| O5—C4—C3 | 120.13 (19) | C10—C8—H8 | 107.3 |
| O5—C4—C5 | 122.0 (2) | C10—C8—C7 | 110.0 (2) |
| O5—C16—H16A | 109.5 | C10—C8—C9 | 110.8 (2) |
| O5—C16—H16B | 109.5 | C11—O7—C7 | 115.47 (17) |
| O5—C16—H16C | 109.5 | C11—N3—C12 | 122.75 (19) |
| O6—C5—C4 | 114.47 (19) | C11—N3—H3 | 114.4 (19) |
| O6—C5—C6 | 125.36 (19) | C12—N3—H3 | 122.3 (19) |
| O6—C17—H17A | 109.5 | C12—C13—H13A | 109.3 |
| O6—C17—H17B | 109.5 | C12—C13—H13B | 109.3 |
| O6—C17—H17C | 109.5 | C12—C13—C14 | 111.8 (2) |

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| O7—C7—C1 | 108.12 (17) | C13—C12—H12A | 108.8 |
| O7—C7—C8 | 108.20 (18) | C13—C12—H12B | 108.8 |
| O7—C7—H7 | 108.7 | C13—C14—H14A | 109.0 |
| O8—C11—O7 | 123.68 (19) | C13—C14—H14B | 109.0 |
| O8—C11—N3 | 126.3 (2) | C14—C13—H13A | 109.3 |
| N3—C12—H12A | 108.8 | C14—C13—H13B | 109.3 |
| N3—C12—H12B | 108.8 | C14—C15—H15A | 109.5 |
| N3—C12—C13 | 113.99 (19) | C14—C15—H15B | 109.5 |
| N3—C11—O7 | 110.05 (18) | C14—C15—H15C | 109.5 |
| C1—C6—H6 | 119.0 | C15—C14—C13 | 112.9 (2) |
| C1—C2—N1 | 120.0 (2) | C15—C14—H14A | 109.0 |
| C1—C2—C3 | 121.2 (2) | C15—C14—H14B | 109.0 |
| C1—C7—C8 | 114.22 (18) | H9A—C9—H9B | 109.5 |
| C1—C7—H7 | 108.7 | H9A—C9—H9C | 109.5 |
| C2—C3—N2 | 119.8 (2) | H9B—C9—H9C | 109.5 |
| C2—C1—C6 | 117.2 (2) | H10A—C10—H10B | 109.5 |
| C2—C1—C7 | 122.5 (2) | H10A—C10—H10C | 109.5 |
| C3—C4—C5 | 117.5 (2) | H10B—C10—H10C | 109.5 |
| C3—C2—N1 | 118.75 (19) | H12A—C12—H12B | 107.7 |
| C4—O5—C16 | 115.31 (19) | H13A—C13—H13B | 107.9 |
| C4—C3—N2 | 118.2 (2) | H14A—C14—H14B | 107.8 |
| C4—C3—C2 | 121.9 (2) | H15A—C15—H15B | 109.5 |
| C5—O6—C17 | 117.76 (18) | H15A—C15—H15C | 109.5 |
| C5—C6—C1 | 121.93 (19) | H15B—C15—H15C | 109.5 |
| C5—C6—H6 | 119.0 | H16A—C16—H16B | 109.5 |
| C6—C1—C7 | 120.26 (19) | H16A—C16—H16C | 109.5 |
| C6—C5—C4 | 120.2 (2) | H16B—C16—H16C | 109.5 |
| C7—C8—H8 | 107.3 | H17A—C17—H17B | 109.5 |
| C8—C7—H7 | 108.7 | H17A—C17—H17C | 109.5 |
| C8—C9—H9A | 109.5 | H17B—C17—H17C | 109.5 |
| C8—C9—H9B | 109.5 | | |

| | | | |
|---|---|---|---|
| O1—N1—C2—C1 | −122.5 (2) | C5—C4—C3—C2 | 4.2 (3) |
| O1—N1—C2—C3 | 53.9 (3) | C6—C1—C2—N1 | 174.4 (2) |
| O2—N1—C2—C1 | 56.9 (3) | C6—C1—C2—C3 | −1.9 (3) |
| O2—N1—C2—C3 | −126.7 (2) | C6—C1—C7—O7 | −36.3 (3) |
| O3—N2—C3—C4 | 56.7 (3) | C6—C1—C7—C8 | 84.2 (2) |
| O3—N2—C3—C2 | −125.9 (3) | C7—O7—C11—O8 | −15.0 (3) |
| O4—N2—C3—C4 | −123.5 (2) | C7—O7—C11—N3 | 165.85 (18) |
| O4—N2—C3—C2 | 53.9 (3) | C7—C1—C6—C5 | −177.8 (2) |
| O5—C4—C3—N2 | 8.2 (3) | C7—C1—C2—N1 | −4.3 (3) |
| O5—C4—C3—C2 | −169.1 (2) | C7—C1—C2—C3 | 179.4 (2) |
| O5—C4—C5—O6 | −8.0 (3) | C9—C8—C7—O7 | 58.3 (3) |
| O5—C4—C5—C6 | 170.6 (2) | C9—C8—C7—C1 | −62.1 (3) |
| N2—C3—C2—N1 | 4.4 (3) | C10—C8—C7—O7 | −66.6 (2) |
| N2—C3—C2—C1 | −179.3 (2) | C10—C8—C7—C1 | 172.9 (2) |
| N3—C12—C13—C14 | −178.41 (19) | C11—O7—C7—C1 | −86.6 (2) |
| C1—C6—C5—O6 | 177.1 (2) | C11—O7—C7—C8 | 149.19 (18) |

| | | | |
|---|---|---|---|
| C1—C6—C5—C4 | −1.4 (3) | C11—N3—C12—C13 | −106.4 (2) |
| C2—C1—C7—O7 | 142.3 (2) | C12—N3—C11—O7 | 176.03 (19) |
| C2—C1—C7—C8 | −97.2 (3) | C12—N3—C11—O8 | −3.1 (4) |
| C2—C1—C6—C5 | 3.6 (3) | C12—C13—C14—C15 | −178.9 (2) |
| C3—C4—C5—O6 | 178.9 (2) | C16—O5—C4—C3 | −110.7 (2) |
| C3—C4—C5—C6 | −2.5 (3) | C16—O5—C4—C5 | 76.3 (3) |
| C4—C3—C2—N1 | −178.3 (2) | C17—O6—C5—C4 | 172.5 (2) |
| C4—C3—C2—C1 | −2.0 (3) | C17—O6—C5—C6 | −6.0 (3) |
| C5—C4—C3—N2 | −178.5 (2) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N3—H3···O8$^{i}$ | 0.78 (3) | 2.26 (3) | 3.042 (3) | 176 (3) |

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