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# Allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside

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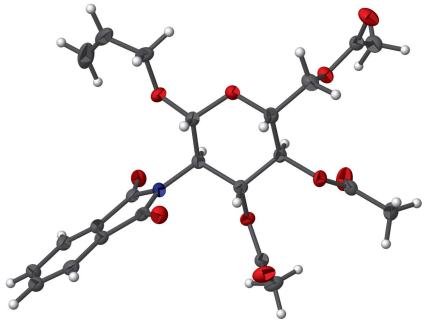
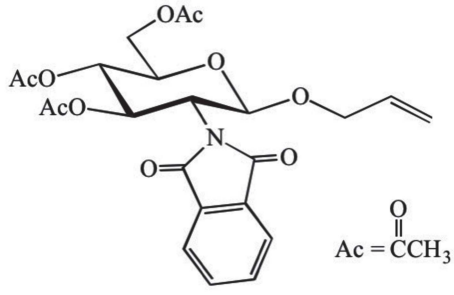
**Structural data**: full structural data are available from iucrdata.iucr.org

The protected glycoside of 2-amino-2-deoxyglucose (glucosamine), namely allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside, $C_{23}H_{25}NO_{10}$, was synthesized from the glycosyl bromide. Crystallographic analysis confirmed the β-anomeric configuration and showed an approximately orthogonal orientation of the phthalimido group with respect to the pyranose ring. The absolute configuration of the molecule was known from the synthetic route and assigned accordingly.

**3D view**



**Chemical scheme**




## Structure description

Aside from its presence in chitin, the second most abundant biopolymer in nature, *N*-acetylglucosamine (GlcNAc) occurs widely in glycans and bioconjugates in both α- and β-linked glycosides as well as in other biologically important substances such as heparins and tunicamycins (Stick & Williams, 2009; Kerns & Wei, 2012; Lindhorst, 2003). Owing to the role of GlcNAc-containing glycosides in biologically active materials and cell surface glycans, there has been much interest in their chemical synthesis (*Ibid*.). The title allyl glycoside (**1**) has been used previously as an intermediate in the synthesis of oligosaccharide haptens of *Streptococci* Group A cell-wall polysaccharides (Pinto *et al.*, 1991) and its analogous *tert*-butyl glycoside was used in a synthetic program aimed at gangliotriosylceramide, a tumor-specific cell-surface marker (Wessel *et al.*, 1984). Our interest in the synthesis of the lipid A disaccharide (Johnson *et al.*, 1999), which is comprised of two β-(1→6) linked GlcNAc units, required the preparation of allyl glycoside **1** for use as an intermediate. The synthesis of **1** was reported using a ferric chloride-catalyzed glycosidation of allyl alcohol with 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (Kiso & Anderson, 1985). Other syntheses have been reported (Miquel *et al.*, 2004). Our route was based on a modification in which the glycosidation of allyl

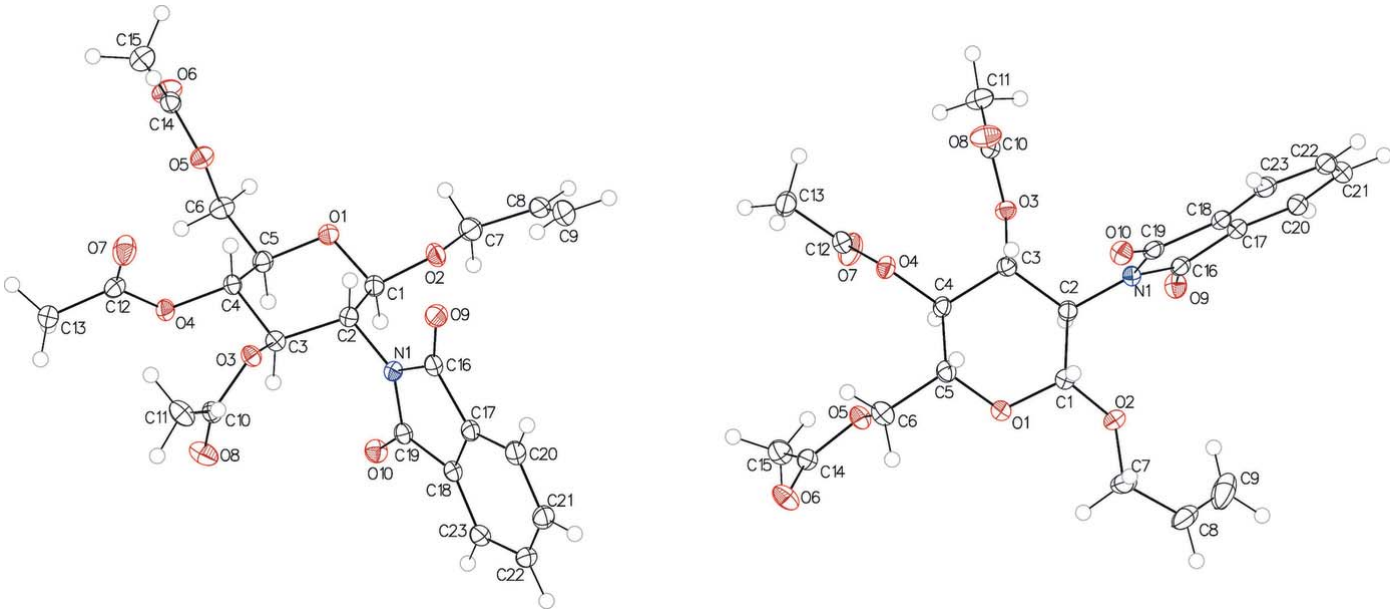



**Figure 1**
Two views of the molecular structure of allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-$\beta$-D-glucopyranoside with displacement ellipsoids at the 40% probability level.

alcohol with 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-$\beta$-D-glucopyranosyl bromide occurred in the presence of silver trifluoromethanesulfonate and tetramethylurea (Hanessian & Banoub, 1977*a*,*b*) in high yield and stereoselectivity. Chromatographic purification of **1** gave product suitable for crystallographic analysis.

The pyranose ring of **1** adopts a chair conformation with little evidence of distortion or puckering (Fig. 1). The N1—C2—C1—O2 and N1—C2—C3—O3 torsion angles are −65.2 (2) and 66.4 (2)°, respectively, corresponding to *gauche* relationships between the C1 allyloxy group and the C2 phthalimido group and between the C2 phthalimido group and the C3 acetoxy group. The phthalimido group is approximately orthogonal to a plane that bisects the pyranose ring at C2 and C5. The stereoselectivity for the formation of the 1,2-*trans* product in glycosidations of sugars that have a phthalimido group at C2 is ascribed to the steric hindrance that this relatively large group provides on the $\alpha$-face of the pyranose ring (Stick & Williams, 2009) or through neighboring group participation involving a phthalimide carbonyl group (Lindhorst, 2003).

## Synthesis and crystallization

*Allyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-$\beta$-D-glucopyranoside* **1**.

To a stirring solution of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-$\beta$-D-glucopyranosyl bromide (0.704 g, 1.41 mmol) (Lemieux *et al.*, 1977) in anhydrous dichloromethane (10 ml) was added allyl alcohol (0.812 g, 0.953 ml, 14 mmol), tetramethylurea (0.205 g, 0.211 ml, 1.77 mmol), and silver trifluoromethanesulfonate (0.398 mg, 1.55 mmol, dried by evaporation from benzene and high vacuum). The flask was wrapped with aluminium foil and the reaction stirred at room temperature. Progress of the reaction was monitored by thin-layer chromatography on aluminium-backed silica gel plates visualized with Hanessian stain. After 3 h dichloromethane (25 ml) was added and solids were removed by filtration through a pad of Celite. The filtrate was transferred to a separatory funnel and washed with saturated aqueous $NaHCO_3$ solution, saturated aqueous NaCl solution, dried ($Na_2SO_4$), and concentrated under reduced pressure to give crude product that was purified by flash chromatography (Still *et al.*, 1978) with 40% ethyl acetate/hexane to give crystalline allyl glycoside; yield, 0.46 g (69%): $R_f$ 0.26 (40% ethyl acetate-hexanes), m.p. 379–381 K, lit. m.p. 382–383 K (Kiso & Anderson, 1985), $[\alpha]_D$ +39.7 (*c*, 1.0, chloroform, lit. $[\alpha]_D$ +37 (*Ibid.*). The $^1$H NMR data for **1** matched that reported (*Ibid.*)

## Refinement

The absolute configuration of the molecule was known from the synthetic route and set consistent with this information. Upon initial refinement, poorly shaped displacement ellipsoids suggested a possible positional disorder of the allyl group. Attempts to refine this disorder were unsuccessful, and so the displacement parameters of allyl group atoms (C7, C8, C9) were refined with the aid of rigid bond restraints and similarity restraints on the anisotropic displacement parameters of nearby atoms, as well as a weak restraint to encourage approximately isotropic behavior. Additional crystal data, data collection and structure refinement details are summarized in Table 1.

**Table 1**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{23}H_{25}NO_{10}$ |
| $M_r$ | 475.44 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 100 |
| $a, b, c$ (Å) | 5.6873 (1), 13.8090 (3), 29.7776 (6) |
| $V$ (Å$^3$) | 2338.61 (8) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.11 |
| Crystal size (mm) | 0.15 × 0.15 × 0.10 |
| | |
| Data collection | |
| Diffractometer | Bruker APEXII CCD |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2014) |
| $T_{min}$, $T_{max}$ | 0.691, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 46038, 5380, 4500 |
| $R_{int}$ | 0.062 |
| (sin $\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.649 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.036, 0.077, 1.03 |
| No. of reflections | 5380 |
| No. of parameters | 310 |
| No. of restraints | 41 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.20, −0.18 |
| Absolute structure | Flack $x$ determined using 1685 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013) |
| Absolute structure parameter | −0.6 (4) |

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

## Acknowledgements

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## References

Bruker (2013). *APEX2* and *SAINT* Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2014). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Hanessian, S. & Banoub, J. (1977*a*). *Carbohydr. Res.* **53**, C13–C16.
Hanessian, S. & Banoub, J. (1977*b*). *Synthetic Methods for Carbohydrates*, ACS Symposium Series; 39, edited by H. S. El Khadem, pp. 36–63. Washington, DC: American Chemical Society.
Johnson, D. A., Keegan, D. S., Sowell, C. G., Livesay, M. T., Johnson, C. L., Taubner, L. M., Harris, A., Myers, K. R., Thompson, J. D., Gustafson, G. L., Rhodes, M. J., Ulrich, J. T., Ward, J. R., Yorgensen, Y. M., Cantrell, J. L. & Brookshire, V. G. (1999). *J. Med. Chem.* **42**, 4640–4649.
Kerns, R. J. & Wei, P. (2012). *Glycobiology and Drug Design*, ACS Symposium Series; 1102, edited by A. A. Klyosov, pp. 235–236. Washington, DC: American Chemical Society.
Kiso, M. & Anderson, L. (1985). *Carbohydr. Res.* **136**, 309–323.
Lemieux, R. U., Takeda, T. & Chung, B. Y. (1977). *Synthetic Methods for Carbohydrates*, ACS Symposium Series; 39, edited by H. S. El Khadem, pp. 90–115. Washington, DC: American Chemical Society.
Lindhorst, T. K. (2003). *Essentials of Carbohydrate Chemistry and Biochemistry*, pp. 97–100 Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA.
Miquel, N., Vignando, S., Russo, G. & Lay, L. (2004). *Synlett*, pp. 0341–0343.
Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* B**69**, 249–259.
Pinto, B. M., Reimer, K. B. & Tixidre, A. (1991). *Carbohydr. Res.* **210**, 199–219.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Stick, R. V. & Williams, S. J. (2009). *Carbohydrates: The Essential Molecules of Life*, pp. 174–177. Oxford, UK; Amsterdam, The Netherlands: Elsevier.
Still, W. C., Kahn, M. & Mitra, A. (1978). *J. Org. Chem.* **43**, 2923–2925.
Wessel, H.-P., Iversen, T. & Bundle, D. R. (1984). *Carbohydr. Res.* **130**, 5–21.

# full crystallographic data

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## Allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-*β*-D-glucopyranoside

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### Allyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-*β*-*D*-glucopyranoside

*Crystal data*

$C_{23}H_{25}NO_{10}$
$M_r$ = 475.44
Orthorhombic, $P2_12_12_1$
$a$ = 5.6873 (1) Å
$b$ = 13.8090 (3) Å
$c$ = 29.7776 (6) Å
$V$ = 2338.61 (8) Å$^3$
$Z$ = 4
$F(000)$ = 1000
$D_x$ = 1.350 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 7270 reflections
$\theta$ = 2.5–23.4°
$\mu$ = 0.11 mm$^{-1}$
$T$ = 100 K
Block, colourless
0.15 × 0.15 × 0.10 mm

*Data collection*

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
Graphite monochromator
Detector resolution: 8 pixels mm$^{-1}$
$\omega$ and $\varphi$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
$T_{min}$ = 0.691, $T_{max}$ = 0.746
46038 measured reflections
5380 independent reflections
4500 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.062
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 1.6°
$h$ = −7→7
$k$ = −17→17
$l$ = −38→38

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.077
$S$ = 1.03
5380 reflections
310 parameters
41 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 0.5249P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.20 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.18 e Å$^{-3}$
Absolute structure: Flack $x$ determined using 1685 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −0.6 (4)

*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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O3 | 0.2553 (3) | 0.46285 (10) | 0.67489 (5) | 0.0204 (3) |
| O5 | 0.5381 (3) | 0.12299 (11) | 0.65519 (5) | 0.0242 (4) |
| O4 | 0.5249 (3) | 0.31082 (11) | 0.71755 (5) | 0.0222 (3) |
| O1 | 0.6786 (3) | 0.28757 (10) | 0.59977 (5) | 0.0231 (4) |
| O10 | 0.8145 (3) | 0.59507 (11) | 0.62906 (5) | 0.0257 (4) |
| O9 | 0.1351 (3) | 0.53828 (12) | 0.55059 (5) | 0.0266 (4) |
| O2 | 0.6391 (3) | 0.38688 (11) | 0.53945 (5) | 0.0277 (4) |
| O6 | 0.7384 (3) | −0.01621 (11) | 0.66104 (6) | 0.0316 (4) |
| O8 | 0.4357 (3) | 0.54328 (14) | 0.73116 (6) | 0.0336 (4) |
| O7 | 0.1550 (3) | 0.25372 (14) | 0.72336 (6) | 0.0379 (5) |
| N1 | 0.4727 (3) | 0.54214 (13) | 0.59438 (6) | 0.0193 (4) |
| C19 | 0.6429 (4) | 0.61102 (16) | 0.60621 (7) | 0.0211 (5) |
| C16 | 0.2979 (4) | 0.58224 (16) | 0.56677 (7) | 0.0206 (5) |
| C2 | 0.4748 (4) | 0.44030 (15) | 0.60714 (7) | 0.0201 (5) |
| H2 | 0.3260 | 0.4107 | 0.5956 | 0.024* |
| C10 | 0.2579 (4) | 0.51553 (16) | 0.71358 (7) | 0.0225 (5) |
| C1 | 0.6795 (4) | 0.38592 (16) | 0.58531 (7) | 0.0226 (5) |
| H1 | 0.8328 | 0.4177 | 0.5926 | 0.027* |
| C14 | 0.5528 (4) | 0.02604 (16) | 0.65995 (8) | 0.0229 (5) |
| C3 | 0.4764 (4) | 0.42761 (15) | 0.65811 (7) | 0.0193 (4) |
| H3 | 0.6093 | 0.4650 | 0.6717 | 0.023* |
| C4 | 0.4985 (4) | 0.32114 (15) | 0.66975 (7) | 0.0196 (5) |
| H4 | 0.3549 | 0.2856 | 0.6595 | 0.023* |
| C17 | 0.3591 (4) | 0.68644 (16) | 0.56204 (7) | 0.0215 (5) |
| C18 | 0.5673 (4) | 0.70329 (16) | 0.58524 (7) | 0.0211 (5) |
| C23 | 0.6683 (4) | 0.79430 (16) | 0.58652 (8) | 0.0255 (5) |
| H23 | 0.8093 | 0.8060 | 0.6027 | 0.031* |
| C5 | 0.7146 (4) | 0.27908 (16) | 0.64710 (7) | 0.0219 (5) |
| H5 | 0.8556 | 0.3181 | 0.6558 | 0.026* |
| C12 | 0.3393 (5) | 0.27364 (16) | 0.74066 (8) | 0.0254 (5) |
| C6 | 0.7580 (4) | 0.17480 (16) | 0.65837 (8) | 0.0255 (5) |
| H6A | 0.8739 | 0.1468 | 0.6372 | 0.031* |
| H6B | 0.8220 | 0.1693 | 0.6892 | 0.031* |
| C21 | 0.3465 (5) | 0.85174 (17) | 0.54017 (8) | 0.0293 (6) |
| H21 | 0.2724 | 0.9038 | 0.5248 | 0.035* |
| C20 | 0.2442 (5) | 0.76010 (16) | 0.53936 (8) | 0.0256 (5) |
| H20 | 0.1010 | 0.7486 | 0.5238 | 0.031* |
| C22 | 0.5556 (5) | 0.86812 (17) | 0.56314 (8) | 0.0294 (6) |
| H22 | 0.6229 | 0.9311 | 0.5629 | 0.035* |
| C15 | 0.3171 (4) | −0.01948 (18) | 0.66364 (9) | 0.0296 (6) |
| H15A | 0.3025 | −0.0514 | 0.6929 | 0.044* |
| H15B | 0.2979 | −0.0675 | 0.6397 | 0.044* |
| H15C | 0.1955 | 0.0304 | 0.6608 | 0.044* |
| C13 | 0.3950 (5) | 0.26533 (18) | 0.78949 (8) | 0.0341 (6) |
| H13A | 0.5642 | 0.2548 | 0.7933 | 0.051* |

| | | | | |
|---|---|---|---|---|
| H13B | 0.3085 | 0.2106 | 0.8023 | 0.051* |
| H13C | 0.3488 | 0.3251 | 0.8049 | 0.051* |
| C11 | 0.0143 (4) | 0.53125 (19) | 0.72999 (8) | 0.0306 (6) |
| H11A | −0.0798 | 0.5614 | 0.7062 | 0.046* |
| H11B | 0.0175 | 0.5738 | 0.7563 | 0.046* |
| H11C | −0.0557 | 0.4689 | 0.7383 | 0.046* |
| C7 | 0.8274 (5) | 0.34770 (18) | 0.51328 (8) | 0.0360 (6) |
| H7A | 0.8399 | 0.2771 | 0.5185 | 0.043* |
| H7B | 0.9780 | 0.3782 | 0.5222 | 0.043* |
| C8 | 0.7798 (7) | 0.3669 (2) | 0.46500 (9) | 0.0510 (9) |
| H8 | 0.8901 | 0.3435 | 0.4436 | 0.061* |
| C9 | 0.5962 (8) | 0.4141 (2) | 0.44989 (10) | 0.0618 (11) |
| H9A | 0.4824 | 0.4386 | 0.4703 | 0.074* |
| H9B | 0.5768 | 0.4238 | 0.4185 | 0.074* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O3 | 0.0195 (8) | 0.0234 (8) | 0.0184 (8) | 0.0030 (7) | −0.0004 (6) | −0.0015 (6) |
| O5 | 0.0216 (8) | 0.0208 (8) | 0.0301 (9) | 0.0019 (7) | −0.0020 (7) | 0.0024 (7) |
| O4 | 0.0251 (8) | 0.0240 (8) | 0.0177 (8) | −0.0017 (7) | −0.0025 (7) | 0.0030 (6) |
| O1 | 0.0285 (9) | 0.0194 (8) | 0.0213 (8) | 0.0015 (7) | 0.0013 (7) | −0.0001 (6) |
| O10 | 0.0230 (9) | 0.0290 (9) | 0.0251 (8) | 0.0002 (7) | −0.0034 (7) | 0.0008 (7) |
| O9 | 0.0262 (9) | 0.0274 (9) | 0.0263 (8) | −0.0031 (7) | −0.0053 (7) | 0.0024 (7) |
| O2 | 0.0382 (10) | 0.0272 (9) | 0.0176 (8) | 0.0039 (8) | 0.0042 (7) | −0.0010 (7) |
| O6 | 0.0239 (9) | 0.0223 (9) | 0.0487 (11) | 0.0042 (7) | −0.0016 (9) | −0.0004 (8) |
| O8 | 0.0266 (9) | 0.0419 (10) | 0.0323 (9) | −0.0017 (8) | −0.0005 (8) | −0.0138 (8) |
| O7 | 0.0304 (10) | 0.0493 (11) | 0.0340 (10) | −0.0106 (9) | −0.0002 (9) | 0.0106 (9) |
| N1 | 0.0216 (9) | 0.0179 (9) | 0.0183 (9) | 0.0003 (8) | −0.0003 (8) | 0.0018 (7) |
| C19 | 0.0223 (12) | 0.0236 (12) | 0.0173 (11) | −0.0004 (9) | 0.0054 (10) | −0.0015 (9) |
| C16 | 0.0225 (12) | 0.0232 (11) | 0.0160 (10) | 0.0015 (10) | 0.0017 (9) | 0.0001 (9) |
| C2 | 0.0217 (11) | 0.0195 (11) | 0.0192 (10) | −0.0003 (9) | −0.0005 (9) | 0.0012 (9) |
| C10 | 0.0278 (12) | 0.0215 (12) | 0.0181 (11) | 0.0032 (10) | −0.0014 (10) | 0.0005 (9) |
| C1 | 0.0277 (12) | 0.0208 (11) | 0.0194 (11) | 0.0013 (9) | 0.0012 (10) | 0.0009 (9) |
| C14 | 0.0258 (12) | 0.0225 (12) | 0.0205 (11) | 0.0018 (10) | −0.0010 (10) | 0.0001 (9) |
| C3 | 0.0180 (10) | 0.0204 (11) | 0.0194 (10) | 0.0020 (9) | −0.0006 (9) | −0.0004 (9) |
| C4 | 0.0226 (11) | 0.0201 (11) | 0.0161 (10) | 0.0001 (9) | −0.0033 (9) | 0.0017 (8) |
| C17 | 0.0245 (11) | 0.0220 (11) | 0.0179 (11) | 0.0004 (10) | 0.0033 (10) | 0.0003 (9) |
| C18 | 0.0243 (11) | 0.0223 (11) | 0.0167 (10) | −0.0003 (9) | 0.0033 (9) | −0.0009 (9) |
| C23 | 0.0299 (12) | 0.0255 (12) | 0.0210 (11) | −0.0033 (10) | 0.0030 (10) | −0.0033 (9) |
| C5 | 0.0225 (12) | 0.0215 (11) | 0.0218 (11) | 0.0012 (9) | −0.0021 (9) | 0.0020 (9) |
| C12 | 0.0318 (13) | 0.0185 (11) | 0.0259 (12) | −0.0013 (10) | 0.0023 (11) | 0.0021 (9) |
| C6 | 0.0209 (11) | 0.0230 (11) | 0.0325 (13) | 0.0001 (10) | −0.0034 (11) | 0.0007 (10) |
| C21 | 0.0404 (14) | 0.0217 (12) | 0.0259 (12) | 0.0065 (11) | 0.0041 (12) | 0.0019 (10) |
| C20 | 0.0294 (12) | 0.0260 (12) | 0.0213 (11) | 0.0056 (11) | 0.0017 (10) | 0.0013 (10) |
| C22 | 0.0428 (15) | 0.0207 (12) | 0.0249 (12) | −0.0051 (11) | 0.0078 (11) | −0.0021 (10) |
| C15 | 0.0247 (13) | 0.0280 (13) | 0.0360 (14) | 0.0009 (10) | 0.0024 (11) | 0.0018 (11) |
| C13 | 0.0537 (17) | 0.0261 (13) | 0.0226 (12) | −0.0088 (12) | 0.0006 (12) | 0.0017 (10) |

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|---|---|---|---|---|---|---|
| C11 | 0.0274 (13) | 0.0401 (15) | 0.0243 (12) | 0.0056 (12) | −0.0004 (10) | −0.0077 (11) |
| C7 | 0.0480 (16) | 0.0289 (14) | 0.0310 (14) | −0.0037 (12) | 0.0175 (13) | −0.0068 (11) |
| C8 | 0.093 (3) | 0.0335 (15) | 0.0264 (15) | −0.0289 (17) | 0.0232 (17) | −0.0101 (12) |
| C9 | 0.110 (3) | 0.051 (2) | 0.0239 (15) | −0.036 (2) | −0.0117 (17) | 0.0047 (14) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| O3—C10 | 1.362 (3) | C17—C20 | 1.385 (3) |
| O3—C3 | 1.438 (3) | C18—C23 | 1.382 (3) |
| O5—C14 | 1.349 (3) | C23—H23 | 0.9500 |
| O5—C6 | 1.444 (3) | C23—C22 | 1.391 (3) |
| O4—C4 | 1.438 (2) | C5—H5 | 1.0000 |
| O4—C12 | 1.360 (3) | C5—C6 | 1.499 (3) |
| O1—C1 | 1.425 (3) | C12—C13 | 1.493 (3) |
| O1—C5 | 1.429 (3) | C6—H6A | 0.9900 |
| O10—C19 | 1.210 (3) | C6—H6B | 0.9900 |
| O9—C16 | 1.208 (3) | C21—H21 | 0.9500 |
| O2—C1 | 1.385 (3) | C21—C20 | 1.393 (3) |
| O2—C7 | 1.431 (3) | C21—C22 | 1.390 (4) |
| O6—C14 | 1.206 (3) | C20—H20 | 0.9500 |
| O8—C10 | 1.201 (3) | C22—H22 | 0.9500 |
| O7—C12 | 1.200 (3) | C15—H15A | 0.9800 |
| N1—C19 | 1.402 (3) | C15—H15B | 0.9800 |
| N1—C16 | 1.404 (3) | C15—H15C | 0.9800 |
| N1—C2 | 1.457 (3) | C13—H13A | 0.9800 |
| C19—C18 | 1.483 (3) | C13—H13B | 0.9800 |
| C16—C17 | 1.487 (3) | C13—H13C | 0.9800 |
| C2—H2 | 1.0000 | C11—H11A | 0.9800 |
| C2—C1 | 1.530 (3) | C11—H11B | 0.9800 |
| C2—C3 | 1.528 (3) | C11—H11C | 0.9800 |
| C10—C11 | 1.485 (3) | C7—H7A | 0.9900 |
| C1—H1 | 1.0000 | C7—H7B | 0.9900 |
| C14—C15 | 1.484 (3) | C7—C8 | 1.487 (4) |
| C3—H3 | 1.0000 | C8—H8 | 0.9500 |
| C3—C4 | 1.516 (3) | C8—C9 | 1.310 (5) |
| C4—H4 | 1.0000 | C9—H9A | 0.9500 |
| C4—C5 | 1.518 (3) | C9—H9B | 0.9500 |
| C17—C18 | 1.391 (3) | | |

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| C10—O3—C3 | 117.72 (17) | O1—C5—H5 | 109.1 |
| C14—O5—C6 | 115.53 (17) | O1—C5—C6 | 108.86 (18) |
| C12—O4—C4 | 117.20 (17) | C4—C5—H5 | 109.1 |
| C1—O1—C5 | 112.05 (16) | C6—C5—C4 | 113.65 (19) |
| C1—O2—C7 | 114.16 (19) | C6—C5—H5 | 109.1 |
| C19—N1—C16 | 111.62 (17) | O4—C12—C13 | 110.9 (2) |
| C19—N1—C2 | 125.71 (18) | O7—C12—O4 | 123.2 (2) |
| C16—N1—C2 | 122.64 (18) | O7—C12—C13 | 125.9 (2) |
| O10—C19—N1 | 125.1 (2) | O5—C6—C5 | 108.59 (18) |

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| O10—C19—C18 | 128.8 (2) | O5—C6—H6A | 110.0 |
| N1—C19—C18 | 106.08 (19) | O5—C6—H6B | 110.0 |
| O9—C16—N1 | 125.3 (2) | C5—C6—H6A | 110.0 |
| O9—C16—C17 | 128.9 (2) | C5—C6—H6B | 110.0 |
| N1—C16—C17 | 105.75 (18) | H6A—C6—H6B | 108.4 |
| N1—C2—H2 | 107.3 | C20—C21—H21 | 119.5 |
| N1—C2—C1 | 111.67 (18) | C22—C21—H21 | 119.5 |
| N1—C2—C3 | 111.70 (17) | C22—C21—C20 | 120.9 (2) |
| C1—C2—H2 | 107.3 | C17—C20—C21 | 117.5 (2) |
| C3—C2—H2 | 107.3 | C17—C20—H20 | 121.2 |
| C3—C2—C1 | 111.17 (18) | C21—C20—H20 | 121.2 |
| O3—C10—C11 | 110.26 (19) | C23—C22—H22 | 119.3 |
| O8—C10—O3 | 123.2 (2) | C21—C22—C23 | 121.4 (2) |
| O8—C10—C11 | 126.5 (2) | C21—C22—H22 | 119.3 |
| O1—C1—C2 | 109.66 (17) | C14—C15—H15A | 109.5 |
| O1—C1—H1 | 110.8 | C14—C15—H15B | 109.5 |
| O2—C1—O1 | 107.83 (17) | C14—C15—H15C | 109.5 |
| O2—C1—C2 | 106.73 (18) | H15A—C15—H15B | 109.5 |
| O2—C1—H1 | 110.8 | H15A—C15—H15C | 109.5 |
| C2—C1—H1 | 110.8 | H15B—C15—H15C | 109.5 |
| O5—C14—C15 | 111.83 (19) | C12—C13—H13A | 109.5 |
| O6—C14—O5 | 122.5 (2) | C12—C13—H13B | 109.5 |
| O6—C14—C15 | 125.7 (2) | C12—C13—H13C | 109.5 |
| O3—C3—C2 | 107.53 (17) | H13A—C13—H13B | 109.5 |
| O3—C3—H3 | 110.2 | H13A—C13—H13C | 109.5 |
| O3—C3—C4 | 108.74 (18) | H13B—C13—H13C | 109.5 |
| C2—C3—H3 | 110.2 | C10—C11—H11A | 109.5 |
| C4—C3—C2 | 109.80 (17) | C10—C11—H11B | 109.5 |
| C4—C3—H3 | 110.2 | C10—C11—H11C | 109.5 |
| O4—C4—C3 | 109.33 (17) | H11A—C11—H11B | 109.5 |
| O4—C4—H4 | 109.8 | H11A—C11—H11C | 109.5 |
| O4—C4—C5 | 108.51 (17) | H11B—C11—H11C | 109.5 |
| C3—C4—H4 | 109.8 | O2—C7—H7A | 109.9 |
| C3—C4—C5 | 109.68 (18) | O2—C7—H7B | 109.9 |
| C5—C4—H4 | 109.8 | O2—C7—C8 | 108.8 (3) |
| C18—C17—C16 | 108.31 (19) | H7A—C7—H7B | 108.3 |
| C20—C17—C16 | 130.3 (2) | C8—C7—H7A | 109.9 |
| C20—C17—C18 | 121.4 (2) | C8—C7—H7B | 109.9 |
| C17—C18—C19 | 108.20 (19) | C7—C8—H8 | 117.8 |
| C23—C18—C19 | 130.5 (2) | C9—C8—C7 | 124.5 (3) |
| C23—C18—C17 | 121.3 (2) | C9—C8—H8 | 117.8 |
| C18—C23—H23 | 121.3 | C8—C9—H9A | 120.0 |
| C18—C23—C22 | 117.4 (2) | C8—C9—H9B | 120.0 |
| C22—C23—H23 | 121.3 | H9A—C9—H9B | 120.0 |
| O1—C5—C4 | 106.90 (17) | | |

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| O3—C3—C4—O4 | −68.6 (2) | C2—C3—C4—O4 | 173.96 (17) |
| O3—C3—C4—C5 | 172.50 (16) | C2—C3—C4—C5 | 55.1 (2) |

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| O4—C4—C5—O1 | 178.04 (16) | C10—O3—C3—C2 | −139.16 (18) |
| O4—C4—C5—C6 | 57.9 (2) | C10—O3—C3—C4 | 102.0 (2) |
| O1—C5—C6—O5 | −73.7 (2) | C1—O1—C5—C4 | 67.7 (2) |
| O10—C19—C18—C17 | 179.9 (2) | C1—O1—C5—C6 | −169.15 (18) |
| O10—C19—C18—C23 | −0.9 (4) | C1—O2—C7—C8 | −171.1 (2) |
| O9—C16—C17—C18 | −177.5 (2) | C1—C2—C3—O3 | −168.13 (17) |
| O9—C16—C17—C20 | 2.1 (4) | C1—C2—C3—C4 | −50.0 (2) |
| O2—C7—C8—C9 | 1.3 (4) | C14—O5—C6—C5 | 173.51 (18) |
| N1—C19—C18—C17 | −0.1 (2) | C3—O3—C10—O8 | 9.0 (3) |
| N1—C19—C18—C23 | 179.1 (2) | C3—O3—C10—C11 | −170.29 (18) |
| N1—C16—C17—C18 | 1.9 (2) | C3—C2—C1—O1 | 52.8 (2) |
| N1—C16—C17—C20 | −178.4 (2) | C3—C2—C1—O2 | 169.36 (17) |
| N1—C2—C1—O1 | 178.30 (17) | C3—C4—C5—O1 | −62.6 (2) |
| N1—C2—C1—O2 | −65.2 (2) | C3—C4—C5—C6 | 177.28 (18) |
| N1—C2—C3—O3 | 66.4 (2) | C4—O4—C12—O7 | −3.4 (3) |
| N1—C2—C3—C4 | −175.45 (18) | C4—O4—C12—C13 | 178.73 (19) |
| C19—N1—C16—O9 | 177.5 (2) | C4—C5—C6—O5 | 45.3 (3) |
| C19—N1—C16—C17 | −2.0 (2) | C17—C18—C23—C22 | −1.0 (3) |
| C19—N1—C2—C1 | −66.5 (3) | C18—C17—C20—C21 | 0.7 (3) |
| C19—N1—C2—C3 | 58.7 (3) | C18—C23—C22—C21 | 1.4 (3) |
| C19—C18—C23—C22 | 179.9 (2) | C5—O1—C1—O2 | −178.89 (17) |
| C16—N1—C19—O10 | −178.6 (2) | C5—O1—C1—C2 | −63.0 (2) |
| C16—N1—C19—C18 | 1.4 (2) | C12—O4—C4—C3 | 108.5 (2) |
| C16—N1—C2—C1 | 111.3 (2) | C12—O4—C4—C5 | −131.9 (2) |
| C16—N1—C2—C3 | −123.5 (2) | C6—O5—C14—O6 | −9.1 (3) |
| C16—C17—C18—C19 | −1.1 (2) | C6—O5—C14—C15 | 170.7 (2) |
| C16—C17—C18—C23 | 179.6 (2) | C20—C17—C18—C19 | 179.2 (2) |
| C16—C17—C20—C21 | −178.9 (2) | C20—C17—C18—C23 | −0.1 (3) |
| C2—N1—C19—O10 | −0.6 (3) | C20—C21—C22—C23 | −0.8 (4) |
| C2—N1—C19—C18 | 179.37 (19) | C22—C21—C20—C17 | −0.3 (3) |
| C2—N1—C16—O9 | −0.6 (3) | C7—O2—C1—O1 | −68.5 (2) |
| C2—N1—C16—C17 | 179.90 (18) | C7—O2—C1—C2 | 173.74 (18) |