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p-Nitrophenyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside

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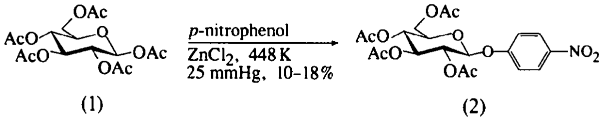
Abstract

The crystal structure of *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside, $C_{20}H_{23}NO_{12}$, was determined in order to ascertain its stereochemistry. The ring adopts a $^3C_5$ chair conformation, with the C3 and O5 atoms at distances of 0.60 (1) and −0.72 (1) Å, respectively, on opposite sides of the C1, C2, C4 and C5 plane. All substituents are in equatorial positions. The carbonyl bonds of the acetyl groups on C2, C3 and C4 are nearly coplanar with their respective ring C—H bonds and point in the same direction.

Comment

In the course of the synthesis of isotopically labelled substrates for lysozyme, we synthesized *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside, (2), *via* a fusion of glucose pentaacetate, (1), and *p*-nitrophenol in the presence of zinc chloride (Jermyn, 1954). This reaction affords a 3:2 α/β ratio of anomeric products, which after repeated fractional crystallization from ethanol afforded the desired β-anomer. Though the melting point (449–452 K) and spectroscopic data were consistent with previously reported data for this compound (m.p. 449 K), an unambiguous proof of the anomeric configuration of this glycoside has not been reported.



(1) (2)

The displacement ellipsoid drawing of the title compound, (2), with the atom-labeling scheme is given in Fig. 1. The absolute configuration of (2) was assigned from the knowledge of the stereochemistry of its synthetic precursor. Each of the non-H substituents on the ring is in an equatorial position. Those on C2 and C4 are on one side of the ring and the rest on the opposite side. The ring is in a $^3C_5$ chair conformation with the C3 and O5 atoms at distances of 0.60 (1) and −0.72 (1) Å, respectively, from the least-squares plane passing through the C1, C2, C4 and C5 atoms. A range of 47.2 (2)–71.5 (2)° is observed for the endocyclic ring torsion angles compared with an angle of 56° in the free cyclohexyl ring (Bucourt, 1974), indicating significant differences in puckering. The puckering of the ring in compound (2) is similar to that of β-D-glucopyranose pentaacetate (Jones, Sheldrick, Kirby & Glenn, 1982), where the endocyclic ring torsion angles range from 45.7 (3) to 63.2 (3)°, the largest difference being in the angle C1—O5—C5—C4 [71.5 (2)°], which is most likely due to the presence of the *p*-nitrophenyl group on C1.

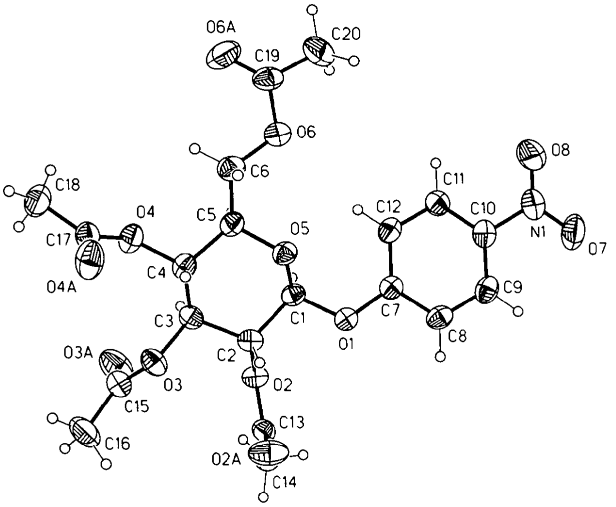


Fig. 1. The molecular structure of (2), with 50% probability ellipsoids, showing the atom-numbering scheme.

In addition to bond lengths and angles, Table 2 lists the ring torsion angles and the torsion angles between the ring C—H bond and C═O bond of each acetyl group on C2, C3 and C4. It can be seen that the C—H and C═O bonds point in the same direction and are approximately coplanar. This appears to be a general trend as evidenced by a search of the October 1995 release of the Cambridge Structural Database (Allen *et al.*, 1991). Both C5—C6 and C1—O1 have *gauche* conformations with respect to the ring O atom, with the O5—C5—C6—O6 and O5—C1—O1—C7 angles being 63.5 (2) and −73.6 (2)°, respectively. Atoms O6 and C7 point towards the volume gap around the ring O atom. The nitro group is nearly coplanar with the phenyl ring and it forms a dihedral angle of 4.3 (5)° with it.

Experimental

Crystals of (2) were obtained by slow evaporation from an ethanol solution.

Crystal data

$C_{20}H_{23}NO_{12}$
$M_r = 469.39$
Monoclinic
$P2_1$
$a = 5.5920\,(1)$ Å
$b = 21.3403\,(5)$ Å
$c = 9.7192\,(2)$ Å
$\beta = 96.197\,(1)°$
$V = 1153.06\,(4)$ Å^3
$Z = 2$
$D_x = 1.352$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4901 reflections
$\theta = 1.5–26.91°$
$\mu = 0.113$ mm^{-1}
$T = 173\,(2)$ K
Needle
0.41 × 0.32 × 0.13 mm
Colorless

Data collection

SMART CCD PLATFORM diffractometer
ω scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.9510$, $T_{\max} = 0.9852$
6121 measured reflections

3573 independent reflections
3371 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0454$
$\theta_{\max} = 26.91°$
$h = -7 \rightarrow 6$
$k = -24 \rightarrow 25$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R(F) = 0.0344$
$wR(F^2) = 0.0909$
$S = 1.124$
3556 reflections
391 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.2707P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.154$ e Å^{-3}
$\Delta\rho_{\min} = -0.137$ e Å^{-3}

Extinction correction: *SHELXTL* (Sheldrick, 1995)
Extinction coefficient: 0.018 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.3 (8)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
O1	−0.6589 (3)	−0.00728 (8)	−0.1738 (2)	0.0345 (4)
O2	−0.6236 (3)	−0.13955 (7)	−0.12414 (14)	0.0326 (3)
O2*A*	−0.2208 (3)	−0.13569 (11)	−0.1110 (2)	0.0571 (5)
O3	−0.5313 (3)	−0.16167 (8)	0.1727 (2)	0.0392 (4)
O3*A*	−0.7451 (4)	−0.24971 (10)	0.1225 (3)	0.0657 (6)
O4	−0.9185 (3)	−0.10309 (9)	0.3114 (2)	0.0401 (4)
O4*A*	−0.6211 (3)	−0.08687 (12)	0.4822 (2)	0.0571 (5)
O5	−0.8058 (3)	0.00410 (8)	0.03510 (15)	0.0331 (3)
O6	−1.1694 (4)	0.06966 (9)	0.1410 (2)	0.0498 (5)
O6*A*	−1.4129 (4)	0.08060 (12)	0.3058 (2)	0.0621 (6)
O7	−1.0094 (4)	0.19195 (11)	−0.6208 (2)	0.0624 (6)
O8	−1.2716 (5)	0.20739 (12)	−0.4773 (2)	0.0700 (7)
N1	−1.0978 (4)	0.18006 (11)	−0.5134 (2)	0.0459 (5)
C1	−0.7830 (4)	−0.03823 (11)	−0.0751 (2)	0.0310 (5)
C2	−0.6268 (4)	−0.09263 (11)	−0.0183 (2)	0.0298 (5)
C3	−0.7215 (4)	−0.12261 (11)	0.1071 (2)	0.0324 (5)
C4	−0.7836 (4)	−0.07350 (11)	0.2113 (2)	0.0333 (5)
C5	−0.9420 (4)	−0.02342 (12)	0.1362 (2)	0.0335 (5)
C6	−1.0138 (5)	0.02815 (13)	0.2277 (3)	0.0423 (6)
C7	−0.7822 (4)	0.03804 (11)	−0.2548 (2)	0.0316 (5)
C8	−0.6768 (4)	0.05472 (12)	−0.3723 (2)	0.0356 (5)
C9	−0.7810 (4)	0.10179 (12)	−0.4581 (2)	0.0375 (5)
C10	−0.9881 (4)	0.12977 (11)	−0.4244 (2)	0.0356 (5)
C11	−1.0943 (4)	0.11376 (12)	−0.3082 (2)	0.0380 (5)
C12	−0.9911 (4)	0.06695 (12)	−0.2215 (2)	0.0380 (5)
C13	−0.4077 (4)	−0.15751 (11)	−0.1616 (2)	0.0336 (5)
C14	−0.4360 (5)	−0.20610 (13)	−0.2718 (3)	0.0413 (5)
C15	−0.5627 (5)	−0.22424 (13)	0.1711 (3)	0.0434 (6)
C16	−0.3440 (6)	−0.2568 (2)	0.2377 (4)	0.0616 (8)
C17	−0.8198 (5)	−0.10493 (12)	0.4451 (2)	0.0394 (5)
C18	−0.9923 (6)	−0.1325 (2)	0.5351 (3)	0.0539 (7)
C19	−1.3617 (5)	0.09302 (12)	0.1932 (3)	0.0430 (6)
C20	−1.4994 (7)	0.1358 (2)	0.0920 (4)	0.0576 (8)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.408 (3)	C1—C2	1.520 (3)
O2—C2	1.437 (3)	C2—C3	1.521 (3)
O3—C3	1.445 (2)	C3—C4	1.523 (3)
O4—C4	1.440 (3)	C4—C5	1.523 (3)
O5—C1	1.417 (3)	C5—C6	1.497 (3)
O5—C5	1.432 (3)		
O1—C1—O5	107.9 (2)	C2—C3—C4	111.5 (2)
O1—C1—C2	107.4 (2)	O4—C4—C5	108.2 (2)
O5—C1—C2	107.9 (2)	O4—C4—C3	108.7 (2)
O2—C2—C1	108.8 (2)	C5—C4—C3	109.1 (2)
O2—C2—C3	108.2 (2)	O5—C5—C6	107.6 (2)
C1—C2—C3	112.1 (2)	O5—C5—C4	106.9 (2)
O3—C3—C2	107.0 (2)	C6—C5—C4	114.2 (2)
O3—C3—C4	108.3 (2)		
C5—O5—C1—C2	−67.3 (2)	C1—O5—C5—C4	71.5 (2)
O5—C1—C2—C3	53.8 (2)	H2—C2···C13—O2*A*	7.0 (2)
C1—C2—C3—C4	−47.2 (2)	H3—C3···C15—O3*A*	5.8 (1)
C2—C3—C4—C5	50.1 (2)	H4—C4···C17—O4*A*	−10.6 (2)

A hemisphere of frames (0.3° in ω) was collected. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability. The C—H distances range from 0.92 (5) to 1.02 (3) Å.

Data collection: *SMART* (Siemens, 1995*a*). Cell refinement: *SMART* and *SAINT* (Siemens, 1995*b*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FR1003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Deoxy-5-*C*-(5-ethoxycarbonyl-1,2,3-triazol-1-yl)-1,2-*O*-isopropylidene-α-D-xylofuranose

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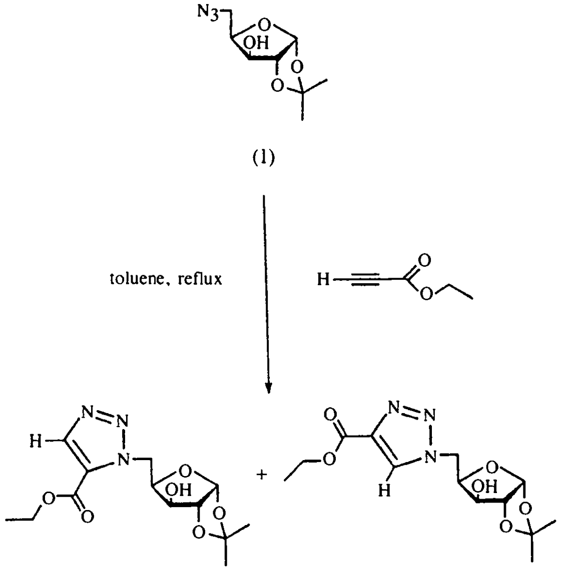
Abstract

Two unrelated molecules of the title compound, ethyl 1-(5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-*C*-yl)-1,2,3-triazole-5-carboxylate, $C_{13}H_{19}N_3O_6$, that are not linked by hydrogen bonding, comprise the asymmetric unit. There are no unusual bond lengths or angles. The two molecules differ in the degree of rotation around the methylene C atom that joins the triazole ring to the sugar part of the molecule. Molecules of the same conformation form infinite chains joined by hydrogen bonding between a H atom on the hydroxyl group of one molecule and an N atom in the triazole ring of another molecule generated by the 2_1 screw axis. Relevant intermolecular N···O distances are 3.013 (3) and 2.806 (3) Å.

Comment

One aspect of our research (Norris, Horton & Levine, 1996) is the addition reaction of sugar-derived azides to alkynes. Such addition reactions generally lead to two products, *e.g.* (2) and (3) (see scheme below). We believe that the major product of this reaction is (3), but a considerable amount of another product (26% yield), which revealed spectroscopic properties almost identical to those of (3), was obtained (Norris, Horton & Levine, 1996). We suspected that the identity of the minor product was indeed (2) and thus undertook an X-ray diffraction study of (2) with the aim of providing proof of the structure of this compound.



(2) (3)

Compound (2) crystallizes with two independent molecules comprising the asymmetric unit. *ORTEP*II (Johnson, 1976) representations of the two molecules (forms 1 and 2) and their atomic labelling schemes are shown in Figs. 1 and 2. The bond lengths and valence angles given in Table 2 are all within the ranges expected for this type of compound. The absolute configuration was assigned to agree with the known chirality of the sugar moiety (*i.e.* α-D-xylofuranose). In fact, this rules out the possibility of the molecule being arranged around a center of inversion since this would result in an inversion at all of the chiral centers in the molecule.

Molecules of the same conformation form infinite chains joined by hydrogen bonding between a H atom on the hydroxyl group of one molecule and an N atom in the triazole ring of another molecule generated by the 2_1 screw axis. The O—H distances in the two hydroxyl groups are similar; O14—H119 0.83 (3) and O24—H219 0.84 (5) Å. The two hydrogen-bond distances are slightly different, however; H119···N13 2.19 (6) and H229···N23 1.99 (5) Å. This may be related to differences in the shape of the two conformers.

There are also some significant differences in the bond distances between the two solid-state forms of (2). For example, the bond lengths O11—C14 of 1.435 (6) and N11—C15 of 1.470 (4) Å in form 1 of compound (2) are significantly longer than the equivalent ones in form 2, namely, O21—C24 of 1.418 (4) and N21—C25 of 1.447 (4) Å. Furthermore, there are also significant differences in some bond

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