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2,3-Di-*O*-benzoyl-1-*O*-*p*-nitrophenyl-6-*O*-pivaloyl-4-*O*-(3′,4′,6′-tri-*O*-acetyl-2′-deoxy-2′-*N*-phthalimido-β-D-1′-glucopyranosyl)-β-D-glucopyranose

KHALIL A. ABBOUD, STAN S. TOPOREK AND BENJAMIN A. HORENSTEIN

Department of Chemistry, University of Florida, PO Box 117200, Gainesville, Florida 32611-7200, USA. E-mail: abboud@chem.ufl.edu

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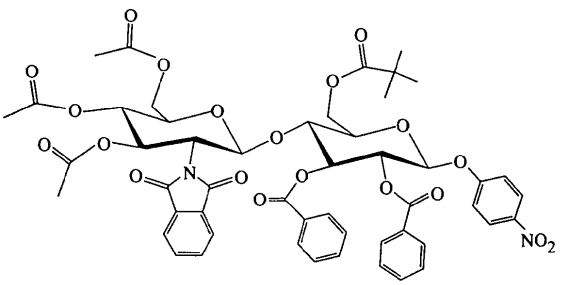
Abstract

The title compound, $C_{51}H_{50}N_2O_{20}$, is an intermediate in the synthesis of a substrate to be used in enzymological studies of lysozyme. It was synthesized *via* a trichloroacetimidate coupling of 2,3,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalimido-1-trichloroacetimidate-β-D-glucopyranoside and *p*-nitrophenyl 2,3-di-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranoside. Both glucose rings adopt chair conformations with one described as $^1C_4$ and the other as $^5C_3$. Atoms C1 and C4 are at distances of 0.727 (4) and −0.652 (4) Å, respectively, and O5′ and C3′ are at distances of 0.713 (4) and −0.555 (5) Å, respectively, from their chair planes.

Comment

In the course of kinetic-isotope-effect method development for lysozyme, we initiated a flexible synthetic route to aryl disaccharide glycosides which would afford site-specific labelled isotopomeric products. We employed the trichloroacetimidate method (Grundler & Schmidt, 1985) to couple 2,3,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalimido-1-trichloroacetimidate-β-D-glucopyranoside with *p*-nitrophenyl 2,3-di-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranoside to afford the desired title compound, (1), in 49% yield. Though the trichloroacetimidate couplings of gluco-configuration glycons are known to afford the β anomer as the major product (Grundler & Schmidt, 1985), the ambiguous spectroscopic data resulted in the need for a crystal structure determination to confirm the stereochemistry of the newly formed glycosidic linkage.



(1)

The anisotropic displacement-ellipsoid drawing of the title compound, (1), with the atom-labelling scheme is shown in Fig. 1. The absolute configuration of (1) was assigned using 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 C1,

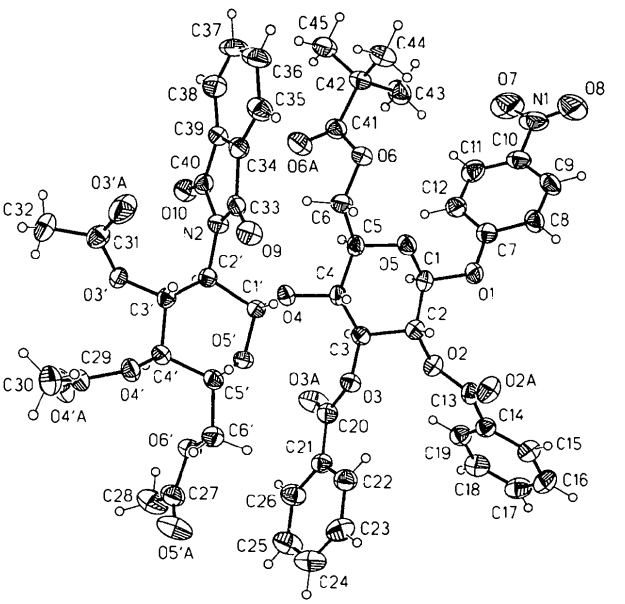


Fig. 1. The molecular structure of (1), with 50% probability ellipsoids, showing the atom-numbering scheme.

C3, C5 and C1′, C3′, C5′ are on one side of the rings containing O5 and O5′, respectively. Both rings adopt chair conformations with the O5-containing ring best described as $^1C_4$ and the O5′-containing ring as $^5C_3$. For the O5 ring, atoms C1 and C4 are at distances of 0.727 (4) and −0.652 (4) Å, respectively, from the plane of atoms C2, C3, C5, O5, while for the O5′ ring, atoms O5′ and C3′ are at distances of 0.713 (4) and −0.555 (5) Å, respectively, from the plane of C1′, C2′, C4′, C5′. Both rings are more puckered than a free cyclohexyl ring where the torsion angles are all 56° (Bucourt, 1974). Endocyclic torsion angles in the O5 ring range from 51.3 (3) to 66.3 (3)°, while in the O5′ ring, the range is from 44.1 (4) to 70.8 (3)°. In comparison, *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (Abboud, Toporek & Horenstein, 1996) has a range of 47.2 (2)–71.5 (2)° and β-D-glucopyranoside pentaacetate (Jones, Sheldrick, Kirby & Glenn, 1982) has a range of 45.7 (3)–63.2 (3)°.

A general trend has been observed where the ring C—H bonds and the C=O bonds in positions β to the ring point in the same direction, and are nearly coplanar. This is also observed in *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside and in a search of the October 1996 release of the Cambridge Structural Database (Allen *et al.* 1991). There is, however, one exception in (1) and that is in angle H3′*A*—C3′···C31—O3′*A* which is 32.6 (2)°. In this instance, the carbonyl O atom, O3′*A*, leans toward the phthalimido five-membered ring. The glycosidic linkage has a similar geometry where both ring C—H bonds point in the same direction and are approximately coplanar, H1′*A*—C1′···C4—H4*A* is 12.06 (3)°.

Experimental

The title compound was prepared in 49% yield by reaction of 2,3,6-tri-*O*-acetyl-2-deoxy-2-*N*-phthalimido-1-trichloroacetimidate-β-D-glucopyranoside with *p*-nitrophenyl 2,3-di-*O*-benzoyl-6-*O*-pivaloyl-β-D-glucopyranoside in dichloromethane/boron trifluoride etherate at 273 K. After work up and chromatography on silica gel, the product was crystallized from ethanol (m.p. 473–474 K).

Crystal data

$C_{51}H_{50}N_2O_{20}$
M_r = 1010.93
Monoclinic
$P2_1$
a = 7.0923 (2) Å
b = 23.1347 (5) Å
c = 15.1181 (3) Å
β = 94.297 (1)°
V = 2473.6 (1) Å^3
Z = 2
D_x = 1.357 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 1.35–25.00°
μ = 0.106 mm^{-1}
T = 173 (2) K
Needle
0.36 × 0.30 × 0.08 mm
Colorless

Data collection

SMART PLATFORM diffractometer
ω scan
Absorption correction: by integration, based on measured crystal faces (*SHELXTL*; Sheldrick, 1995)
T_{min} = 0.967, T_{max} = 0.992
15 459 measured reflections
7143 independent reflections
5991 reflections with $I > 2\sigma(I)$
R_{int} = 0.0357
θ_{max} = 25°
$h = -9 \rightarrow 9$
$k = -22 \rightarrow 29$
$l = -17 \rightarrow 19$

Refinement

Refinement on F^2
$R(F)$ = 0.0450
$wR(F^2)$ = 0.1201
S = 1.044
7125 reflections
659 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.5645P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.02
$\Delta\rho_{max}$ = 0.227 e Å^{-3}
$\Delta\rho_{min}$ = −0.225 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0083 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.4 (8)

Table 1. *Selected geometric parameters (Å, °)*

O4—C1′	1.394 (4)	C1′—C2′	1.540 (4)
O4—C4	1.444 (4)	C2—C3	1.533 (4)
O5—C1	1.403 (4)	C2′—C3′	1.526 (4)
O5—C5	1.433 (4)	C3—C4	1.531 (4)
O5′—C1′	1.424 (4)	C3′—C4′	1.514 (4)
O5′—C5′	1.429 (4)	C4—C5	1.528 (4)
C1—C2	1.515 (4)	C4′—C5′	1.534 (4)
C1′—O4—C4	117.6 (2)	C4—C3—C2	109.9 (3)
C1—O5—C5	113.5 (2)	C4′—C3′—C2′	113.9 (3)
C1′—O5′—C5′	111.4 (2)	O4—C4—C5	106.4 (2)
O5—C1—C2	108.4 (2)	O4—C4—C3	110.6 (2)
O4—C1′—O5′	107.9 (2)	C5—C4—C3	110.0 (2)
O4—C1′—C2′	108.1 (2)	C3′—C4′—C5′	109.4 (2)
O5′—C1′—C2′	108.4 (2)	O5—C5—C4	110.4 (2)
C1—C2—C3	106.8 (2)	O5′—C5′—C4′	107.8 (2)
C3′—C2′—C1′	111.7 (2)		

Although the Flack parameter refines to a value of −0.4 (8), its large error renders it indeterminate as to the absolute configuration of the title compound whose configuration is known from the stereochemistry of the starting material. The H atoms were placed in idealized positions and were refined riding on their parent atoms. C—H distances of 0.96 and 0.97 Å were used for methyl and secondary C atoms, respectively. A distance of 0.93 Å was used for C_{sp^2} atoms. The H-atom displacement parameters were assigned to be $1.2U_{eq}$ of the parent C atom and $1.5U_{eq}$ for the methyl atoms. 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.

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

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equipment. BAH wishes to acknowledge the National Science Foundation for receipt of a CAREER award.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1246). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N,N-Diacetyl-2,5-dimethyl-6-nitroaniline†

ALAN R. KENNEDY AND ABEDAWN I. KHALAF

Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland. E-mail: a.r.kennedy@ccsun.strath.ac.uk

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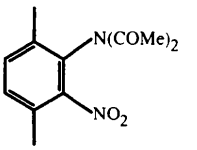
Abstract

The diacetylamino moiety of the title compound, $C_{12}H_{14}N_2O_4$, is shown to adopt a *syn–anti* conformation and is twisted away from the perpendicular to the aryl ring.

Comment

During ongoing research on heterocyclic compounds with medicinal activity, the synthesis of *N*-acetyl-2,5-dimethyl-6-nitroanilide was sought (Suzuki, Ishibashi, Murashima & Tsukamoto, 1991; Sotomatsu, Shigemura, Murata & Fujita, 1993). No reaction took place between 2,5-dimethyl-6-nitroaniline and acetic anhydride at room temperature, but on heating overnight *N,N*-diacetyl-2,5-dimethyl-6-nitroaniline, (I), was produced, with no traces of the monoacetylated product. The crystal structure determination was undertaken in order to gain information on the conformation of the diacetylaniline fragment.



(I)

The crystal structure of (I) was found to consist of discrete molecules, with no intermolecular contacts significantly less than the sum of van der Waals radii. The internal angles of the highly substituted benzene ring display wide variations from trigonal geometry. The range is 115.6 (3)–123.3 (3)° (Table 1) which can be explained by the inductive effects of the substituents (Domenicano, 1992). Similarly the aryl ring bond distances span the range 1.364 (6)–1.392 (4) Å. The widening of the C(2)—C(1)—C(6) angle observed in *p*-bis-(diacetylamino)benzene (Beagley, Flowers, Hafees & Pritchard, 1987) is cancelled in (I) by the large inductive effect of the *ortho*-NO_2 group.

As may be expected, atoms C(10), O(1), C(9), N(1) and C(11) in compound (I) are coplanar, while a twist about the N(1)—C(11) bond displaces the O(2) and C(12) atoms from this plane (Table 1. The diacetylamino (DAA) group adopts a *syn–anti* conformation with respect to the aryl ring and is shifted away from the perpendicular to the ring plane [C(2)—C(1)—N(1)—C(9) −104.0 (4) and C(2)—C(1)—N(1)—C(11) 77.9 (4)°]. A search of the Cambridge Structural Database (Allen & Kennard, 1993) found further structures (Irving & Irving, 1989; Reboul, Pepe, Siri, Odden, Rahal, Soyfer & Barbe, 1992; Reboul, Rahal, Pepe, Odden, Siri, Astier, Soyfer & Barbe, 1992; Wieckowski & Kry-

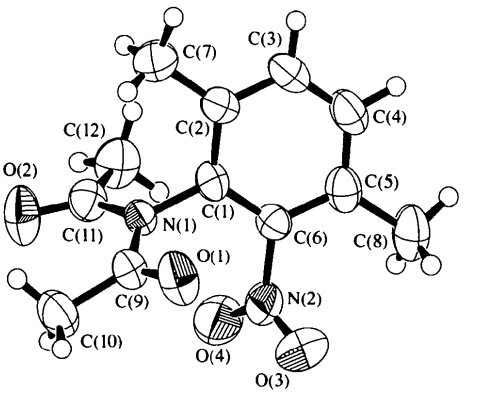


Fig. 1. The molecular structure of compound (I) with the atomic numbering. Non-H atoms are shown as 50% probability ellipsoids and H atoms as small spheres of arbitrary size.

† Alternative name: 3,6-dimethyl-2-nitrophenyldiacetamide.