Acta Cryst. (1981). B37, 963–966

Structure of 1,2,3-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-triphenylmethyl-α-D-glucopyranose (6′-*O*-Trityl-α-cellobiose Heptaacetate)

By Tooru Taga, Shigeyuki Sumiya and Kenji Osaki

Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606, *Japan*

and Toshiko Utamura and Kyoko Koizumi

Faculty of Pharmaceutical Sciences, Mukogawa Women's University, 4-16 *Edagawa, Nishinomiya* 663, *Japan*

(*Received* 29 *August* 1980; *accepted* 24 *November* 1980)

Abstract. $C_{45}H_{50}O_{18}$, monoclinic, $P2_1$, $a = 22{\cdot}70\,(13)$, $b = 9{\cdot}11\,(6)$, $c = 12{\cdot}56\,(9)$ Å, $\beta = 108{\cdot}4\,(4)^\circ$, $V = 2464{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}184$ Mg m^{-3}, $\mu = 0{\cdot}99$ mm^{-1}, λ(Mo $K\alpha$) = 0·70926 Å. The structure was refined to $R = 0{\cdot}088$ for 2337 observed reflexions. The torsion angles around the β 1→4 glycosidic bonds are 131·7 (9)° for C(1)—O(1)—C(4′)—C(3′) and 158·0 (8)° for C(2)—C(1)—O(1)—C(4′). A short O(3′)···O(5) non-bonding contact [3·34 (2) Å] was observed between the two glucopyranosyl residues. The trityl group on the reducing residue (primed) has an intramolecular van der Waals contact with the non-reducing residue (unprimed).

Introduction. The molecular conformation of the title compound, which was prepared from cellobiose (Koizumi & Utamura, 1978), has received attention, particularly with respect to the torsion angles about the β 1→4 glycosidic bonds in relation to the structures of polysaccharides, β 1→4 glucans. A transparent single crystal was obtained by recrystallization from ethanol. The reflexion data were collected on a four-circle diffractometer with monochromatized Mo $K\alpha$ radiation, using a spherical crystal (0·24 mm diameter). The unit-cell parameters were refined by the least-squares method using 15 high-angle reflexions, and the intensity data were collected by means of the ω–2θ scanning technique with a scan rate of 4° (ω) min^{-1}. The structure was solved by the direct method with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1977). The complete structure was obtained by successive Fourier syntheses. All H atoms, except for those of the acetyl groups, were revealed in the difference Fourier maps. The anisotropic block-diagonal least-squares refinement reduced the R value to 0·088 for 2337 observed reflexions [$F/\sigma(F) > 3{\cdot}0$]. Atomic scattering factors of all atoms were obtained from *International Tables for X-ray Crystallography* (1974). The final structure parameters are listed in Tables 1 and 2.* The molecular and crystal structures are depicted in Figs. 1 and 2 respectively. The atomic

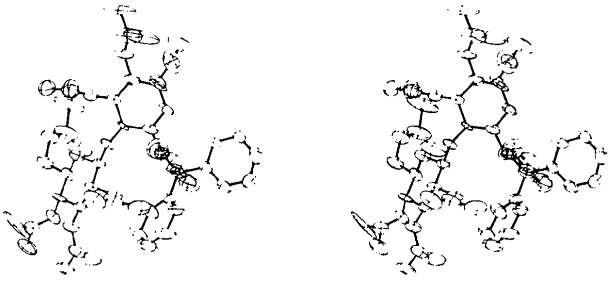

Fig. 1. A stereoscopic view of the molecule down the *b* axis.

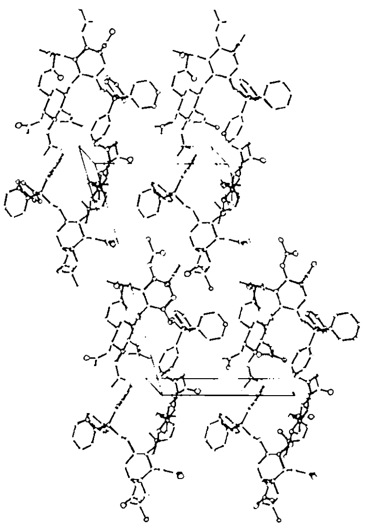

Fig. 2. A perspective drawing of the crystal structure. Axes for the unit cell are **a**↑, **c**→, and **b** is out of the page.

---

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35819 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0567-7408/81/040963-04$01.00

Table 1. *Fractional atomic coordinates* (×10⁴) *and thermal parameters of the non-hydrogen atoms with estimated standard deviations in parentheses*

The thermal parameters are the isotropic equivalents of the anisotropic thermal parameters (Hamilton, 1959).

	x	y	z	B_{eq} (Å^2)
C(1)	2442 (5)	2708 (15)	6 (9)	3·28
C(2)	1883 (5)	3523 (15)	−805 (10)	3·07
C(3)	1351 (5)	2417 (17)	−1367 (9)	3·65
C(4)	1581 (5)	1137 (17)	−1910 (10)	3·95
C(5)	2183 (6)	447 (16)	−1041 (10)	3·90
C(6)	2465 (6)	−741 (17)	−1642 (11)	4·69
C(7)	1524 (7)	6023 (19)	−557 (12)	5·57
C(8)	1353 (8)	7030 (20)	254 (17)	7·27
C(9)	265 (6)	3137 (20)	−2310 (12)	5·34
C(10)	−159 (7)	4092 (24)	−3250 (13)	7·01
C(11)	838 (7)	−355 (24)	−3247 (12)	6·54
C(12)	367 (8)	−1664 (23)	−3399 (13)	7·53
C(13)	3216 (7)	−1846 (18)	−27 (14)	6·41
C(14)	3909 (8)	−2149 (23)	554 (18)	9·67
O(1)	2935 (3)	3709 (0)	451 (6)	3·34
O(2)	1665 (4)	4595 (10)	−145 (7)	3·58
O(3)	874 (4)	3238 (11)	−2249 (7)	4·45
O(4)	1111 (4)	−19 (12)	−2193 (7)	4·81
O(5)	2640 (4)	1590 (10)	−637 (7)	4·09
O(6)	3105 (5)	−1143 (12)	−981 (8)	5·74
O(7)	1540 (6)	6353 (14)	−1499 (9)	7·75
O(9)	84 (5)	2399 (19)	−1694 (10)	9·53
O(11)	907 (7)	348 (24)	−4028 (10)	17·04
O(13)	2809 (5)	−2179 (16)	398 (10)	8·64
C(1′)	4406 (6)	4288 (21)	3411 (10)	5·48
C(2′)	4533 (6)	3219 (19)	2548 (11)	4·64
C(3′)	4043 (5)	3462 (16)	1410 (10)	3·56
C(4′)	3390 (5)	3268 (14)	1504 (8)	2·34
C(5′)	3316 (5)	4292 (14)	2459 (9)	3·18
C(6′)	2708 (6)	4018 (16)	2690 (11)	3·87
C(7′)	4997 (8)	6654 (27)	3831 (14)	8·43
C(8′)	4983 (11)	8270 (21)	3488 (16)	9·51
C(9′)	5622 (9)	2781 (26)	3111 (16)	9·10
C(10′)	6249 (7)	3178 (29)	2950 (19)	10·87
C(11′)	4251 (7)	2812 (18)	−311 (12)	5·39
C(12′)	4313 (8)	1464 (22)	−1023 (14)	7·29
C(13′)	2240 (6)	2119 (15)	3592 (10)	3·51
C(14′)	2326 (6)	432 (15)	3889 (11)	3·42
C(15′)	1967 (8)	−233 (18)	4463 (13)	5·85
C(16′)	2050 (8)	−1746 (22)	4729 (13)	6·48
C(17′)	2490 (10)	−2647 (20)	4472 (14)	7·83
C(18′)	2839 (10)	−1935 (19)	3886 (18)	9·26
C(19′)	2770 (9)	−452 (17)	3600 (15)	6·56
C(20′)	1572 (6)	2405 (18)	2739 (10)	4·36
C(21′)	1279 (8)	1284 (21)	1969 (13)	6·53
C(22′)	701 (8)	1538 (25)	1112 (13)	8·26
C(23′)	426 (7)	2977 (26)	1017 (14)	8·00
C(24′)	720 (7)	4064 (25)	1750 (14)	7·25
C(25′)	1291 (6)	3847 (19)	2604 (11)	4·79
C(26′)	2378 (6)	2949 (16)	4736 (10)	3·80
C(27′)	1913 (6)	3419 (18)	5199 (10)	4·71
C(28′)	2057 (7)	4113 (18)	6236 (12)	5·32
C(29′)	2676 (8)	4355 (21)	6825 (12)	7·18
C(30′)	3161 (7)	3961 (21)	6431 (11)	5·53
C(31′)	2992 (6)	3236 (18)	5353 (11)	4·59
O(1′)	4503 (4)	5805 (13)	3138 (7)	5·58
O(2′)	5157 (4)	3554 (12)	2455 (7)	5·10
O(3′)	4134 (4)	2373 (11)	646 (7)	4·20
O(5′)	3809 (4)	4113 (12)	3491 (6)	4·51
O(6′)	2695 (3)	2502 (10)	3039 (7)	3·47
O(7′)	5410 (6)	6000 (21)	4615 (12)	11·91
O(9′)	5586 (6)	1938 (21)	3843 (14)	13·53
O(11′)	4290 (6)	4101 (15)	−543 (9)	8·10

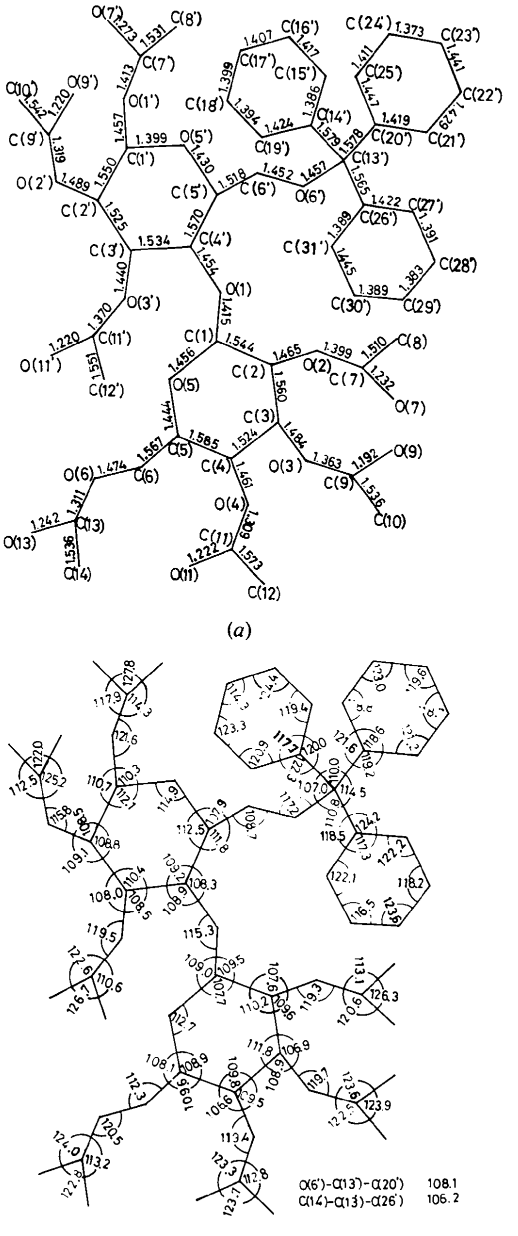

Fig. 3. A schematic diagram of the molecule showing (*a*) atomic numbering and bond lengths (Å), and (*b*) bond angles (°). The e.s.d.'s of the bond lengths range from 0·014 to 0·32 Å, and of the bond angles from 0·8 to 2·0°.

numbering, and bond lengths and bond angles are given in Fig. 3.

Discussion. As is evident in Fig. 1, the two pyranose rings have the normal $^4C_1$ conformation. The bond lengths and angles in the pyranose rings are in good agreement with the average values for α- and β-pyranoses determined to date (Jeffrey & French, 1978). Table 3 lists the bond lengths, bond angles and torsion

Table 2. *Atomic coordinates* (×10³) *of the hydrogen atoms, except for those of acetyl groups, with estimated standard deviations in parentheses*

	x	*y*	*z*		*x*	*y*	*z*
H(1)	229 (5)	215 (14)	60 (9)	H(15′)	165 (5)	32 (14)	472 (9)
H(2)	203 (5)	405 (15)	−136 (9)	H(16′)	175 (5)	−226 (14)	504 (9)
H(3)	120 (5)	206 (14)	−76 (9)	H(17′)	249 (5)	−371 (14)	468 (9)
H(4)	170 (5)	148 (14)	−261 (9)	H(18′)	312 (5)	−255 (14)	367 (9)
H(5)	208 (5)	−4 (15)	−38 (9)	H(19′)	301 (5)	2 (14)	315 (9)
H(6,1)	219 (5)	−167 (15)	−175 (9)	H(21′)	147 (5)	17 (14)	198 (9)
H(6,2)	247 (5)	−30 (14)	−241 (9)	H(22′)	52 (5)	72 (14)	54 (9)
H(1′)	472 (5)	403 (15)	414 (9)	H(23′)	3 (5)	325 (14)	45 (9)
H(2′)	452 (5)	216 (14)	285 (9)	H(24′)	53 (5)	506 (14)	171 (9)
H(3′)	410 (5)	449 (14)	113 (9)	H(25′)	149 (5)	464 (14)	310 (9)
H(4′)	333 (5)	217 (14)	166 (9)	H(27′)	147 (5)	321 (14)	473 (9)
H(5′)	330 (5)	530 (14)	214 (9)	H(28′)	172 (5)	442 (14)	654 (9)
H(6,1′)	272 (5)	472 (14)	333 (9)	H(29′)	277 (5)	484 (14)	753 (9)
H(6,2′)	234 (5)	432 (14)	206 (9)	H(30′)	363 (5)	421 (14)	695 (9)
				H(31′)	332 (5)	295 (14)	506 (9)

Table 3. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *about β* 1 → 4 *glycosidic bonds in β-cellobiose and its derivatives*

	β-Cellobiose	Methyl β-cellobioside	β-Cellobiose peracetate	This work
C(1)–O(1)	1·397 (4)	1·390 (5)	1·382 (15)	1·415 (14)
C(4′)–O(1)	1·446 (4)	1·437 (5)	1·450 (15)	1·454 (14)
C(1)–O(1)–C(4′)	116·1 (2)	115·8 (3)	116·8 (7)	115·3 (8)
C(1)–O(1)–C(4′)–C(3′)	106·4	80·3	133·5	131·7 (9)
C(1)–O(1)–C(4′)–C(5′)	−132·3	−160·7	−103·8	−109·7 (9)
C(4′)–O(1)–C(1)–C(2)	166·5	152·0	165·2	158·0 (9)
C(4′)–O(1)–C(1)–O(5)	−76·3	−91·1	−77·1	−84·4 (11)

angles around the β 1 → 4 glycosidic bonds with the corresponding values for β-cellobiose (Chu & Jeffrey, 1968), methyl β-cellobioside (Ham & Williams, 1970), and β-cellobiose peracetate (Leung, Chanzy, Pérez & Marchessault, 1976). The anomeric C(1)–O(1) bond is significantly shorter than C(4′)–O(1). The difference of 0·041 Å agrees with those of the other three within experimental errors. Although the C(1)–O(1)–C(4′) bond angle of 115·3(8)° in the title compound is smaller than for the other three compounds, the C(1)···C(4′) distances are in good agreement throughout the four compounds. The torsion angles around C(1)–O(1) and C(4′)–O(1) most resemble those of β-cellobiose peracetate. The largest disagreement of the torsion angles from those of β-cellobiose and methyl β-cellobioside is found in the angle about bond C(4′)–O(1). This disagreement may be caused by the O(3′)···O(5) intramolecular hydrogen bond formed in the unacetylated cellobioses. O(3′) and O(5) in the present compound have a short contact [3·34 (2) Å], but they are unable to form a hydrogen bond.

The torsion angles O(5)–C(5)–C(6)–O(6) and C(4)–C(5)–C(6)–O(6) are 46·3 (14) and 164·9 (10)° respectively (*gauche–trans*). The corresponding angles in the primed moiety are −64·0 (12) and 60·3 (11)° (*gauche–gauche*). The *gt–gg′* conformation for the whole molecule differs from the *gt–gt′* of β-cellobiose and from the *gg–gt′* of β-cellobiose peracetate. The energy difference between the *gt* and *gg* conformations may, therefore, be small as estimated by Sundaralingam (1968). The torsion angle C(5′)–C(6′)–O(6′)–C(13′) is 163·5 (8)°. The bulky trityl group approaches the unprimed pyranose moiety; C(24′) has the shortest C···C nonbonding contact [3·82 (3) Å] with C(8) and the shortest C···O nonbonding contact [3·71 (3) Å] with O(2). The intramolecular van der Waals interactions between these atoms may contribute to stabilize the *gg′* conformation about the C(5′)–C(6′) bond.

All acetyl groups have good planarity, and the deviation of each atom from the mean plane is less than 0·04 Å. The H–C–O–C (acetyl) bond in each acetyl group has the usual eclipsed form (Leung & Marchessault, 1973), except for that of the O(6) acetyl group. In this form the O(C=O) atom approaches the ring H atom (2·30–2·44 Å). Even at the O(6) acetyl group the O(C=O) atom is close to the ring H(5) atom (2·55 Å). Thus the attractive interactions between these O and H atoms must make a large contribution to the stability of the established acetyl conformation. The torsion angle C(5)–C(6)–O(6)–C(13) is 67·5 (15)°. This *gauche* conformation is unique for the acetyl groups whose ester oxygen takes a *gt* position about the C(5)–C(6) bond. The same conformation has been found twice before, *viz* in β-cellobiose peracetate (Leung, Chanzy, Pérez & Marchessault, 1976) and 6-*O*-acetylglucopyranose (Lindberg, 1976). As indicated in Fig. 2, the molecules are packed in the structure with van der Waals contacts. The O(6) acetyl group is approached by the O(2) acetyl group of the neighbouring molecules which are packed along the *b* axis. The shortest intermolecular distance [3·23 (3) Å] is found between C(7) and O(13) of these groups. Such packing interactions may have some effects on the side-chain conformations, especially on the O(6) acetyl conformation.

We thank Professor Nobuo Morimoto and Dr Katsutoshi Tomita, Institute of Geology and Mineralogy, Faculty of Science, Kyoto University, for the use of the Rigaku AFC5 diffractometer. All computations were performed on the Facom M190 computer at Data Processing Center, Kyoto University, using the *KPAX* program system.

References

Chu, S. C. & Jeffrey, G. A. (1968). *Acta Cryst.* B**24**, 830–838.
Ham, J. T. & Williams, D. G. (1970). *Acta Cryst.* B**26**, 1373–1385.
Hamilton, W. C. (1959). *Acta Cryst.* **12**, 609–610.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Jeffrey, G. A. & French, A. D. (1978). *Molecular Structure by Diffraction Methods*, Vol. 6, edited by L. E. Sutton & M. R. Truter, pp. 183–223. Spec. Publ. The Chemical Society, London.
Koizumi, K. & Utamura, T. (1978). *Yakugaku Zasshi*, **98**, 327–334.
Leung, F., Chanzy, H. D., Pérez, S. & Marchessault, R. H. (1976). *Can. J. Chem.* **54**, 1365–1371.
Leung, F. & Marchessault, R. H. (1973). *Can. J. Chem.* **51**, 1215–1222.
Lindberg, K. B. (1976). *Acta Cryst.* B**32**, 642–645.
Main, P., Woolfson, M. M., Lessinger, L., Germain, G. & Declercq, J. P. (1977). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Sundaralingam, M. (1968). *Biopolymers*, **6**, 189–213.

Acta Cryst. (1981). B**37**, 966–969

Tetraphenyldiphosphine Disulphide (Tetraphenyl-1,2-dithioxodi-λ^5-phosphane), $Ph_2P(S)P(S)Ph_2$*

By A. J. Blake, R. A. Howie and G. P. McQuillan†

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland

(*Received* 19 *September* 1980; *accepted* 22 *December* 1980)

Abstract. $C_{24}H_{20}P_2S_2$, monoclinic, $P2_1/c$, $a = 9{\cdot}628$ (3), $b = 15{\cdot}798$ (11), $c = 14{\cdot}304$ (4) Å, $\beta = 96{\cdot}29$ (3)°, $V = 2162{\cdot}6$ (17) Å^3, $D_o = 1{\cdot}38$ (displacement), $D_c = 1{\cdot}34$ Mg m^{-3}, $Z = 4$. The final R is 0·045 for 2259 reflections. The unit cell contains two independently oriented pairs of *trans*-$Ph_2P(S)P(S)Ph_2$ molecules in two sets of (C_i) special positions. The P—P bond [2·263 (4) Å (mean)] is significantly longer than that found (2·21 Å approximately) in corresponding alkyl compounds.

Introduction. The IR spectrum of tetraphenyldiphosphine disulphide contains only one identifiable SPPS stretching absorption, assigned to υ_{as}PS, and is consistent with a planar *trans* SPPS conformation similar to that found in various related tetraalkyl compounds (Cowley & White, 1966). The highest-symmetry conformation possible for an $R_2P(S)P(S)R_2$ molecule is C_{2h}, but in practice this appears to be achieved only in the tetramethyl compound (Pedone & Sirigu, 1967; Lee & Goodacre, 1971). In other compounds for which detailed structural information is available [tetraethyldiphosphine disulphide (Dutta & Woolfson, 1961); bis(cyclotetramethylene)diphosphine disulphide (Lee & Goodacre, 1969); bis(cyclopentamethylene)diphosphine disulphide (Lee & Goodacre, 1970)] the alkyl groups are not symmetrically oriented relative to the SPPS plane and the molecules belong to the C_i point group. The C_{2h} and C_i conformations cannot be distinguished reliably using vibrational data alone and crystallographic analysis of the tetraphenyl compound was therefore desirable in order to confirm the proposed *trans* structure, to determine the orientation of the phenyl groups and to provide information for a more detailed examination of the vibrational spectrum.

Tetraphenyldiphosphine disulphide was prepared as colourless square prismatic, almost cubic, crystals from the reaction of tetraphenyldiphosphine with sulphur

---

* Diphosphine derivatives. VII. Part VI: Blake, McQuillan & Oxton (1980).

† To whom correspondence should be addressed.

0567-7408/81/040966-04$01.00