C(6)	0.7754 (6)	0.2738 (6)	0.2962 (4)	0.023 (2)
C(7)	0.6358 (6)	0.1976 (6)	0.3262 (4)	0.026 (2)
C(8)	0.9466 (5)	0.5259 (5)	0.2559 (4)	0.019 (2)
C(9)	1.0380 (6)	0.4073 (6)	0.1970 (4)	0.026 (2)
C(10)	1.0739 (6)	0.6080 (6)	0.3698 (4)	0.027 (2)
C(11)	0.8821 (5)	0.6449 (5)	0.1696 (4)	0.019 (2)
C(12)	0.7515 (5)	0.5902 (5)	0.0690 (4)	0.021 (2)
C(13)	0.6925 (5)	0.6922 (5)	−0.0134 (4)	0.021 (2)
C(14)	0.7684 (6)	0.8509 (6)	0.0050 (4)	0.022 (2)
C(15)	0.8983 (6)	0.9095 (5)	0.1018 (4)	0.023 (2)
C(16)	0.9548 (5)	0.8067 (6)	0.1843 (4)	0.022 (2)
O(3)	0.7117 (4)	0.9488 (4)	−0.0853 (3)	0.024 (1)
O(4)	0.6515 (4)	1.1393 (4)	0.0364 (3)	0.032 (1)
C(17)	0.6589 (6)	1.0892 (6)	−0.0545 (4)	0.026 (2)
Cl(2)	0.6061 (2)	1.1890 (2)	−0.1781 (1)	0.035 (1)

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

Cl(1)—C(1)	1.762 (5)	C(15)—C(16)	1.387 (7)
C(1)—O(1)	1.177 (5)	O(3)—C(17)	1.359 (6)
C(1)—O(2)	1.310 (6)	O(4)—C(17)	1.162 (7)
O(2)—C(2)	1.445 (6)	C(17)—Cl(2)	1.742 (5)
C(14)—O(3)	1.424 (6)		
Cl(1)—C(1)—O(2)	107.3 (3)	C(14)—O(3)—C(17)	116.5 (4)
O(1)—C(1)—O(2)	130.3 (5)	O(3)—C(17)—O(4)	128.2 (5)
C(1)—O(2)—C(2)	116.7 (3)	O(3)—C(17)—Cl(2)	107.2 (4)
C(5)—C(8)—C(11)	109.2 (3)		

The crystal was sealed in a glass capillary under dry nitrogen because of its moisture sensitivity. Data were collected using Siemens *R3m/V* software. The structure was solved by direct methods and refined using the *SHELXTL-Plus* (Sheldrick, 1988) program package on a MicroVAX II computer. H atoms were placed in idealized positions and constrained to C—H = 0.96 Å with isotropic displacement parameters $U = 0.08$ Å^2. All non-H atoms were treated as anisotropic. *SHELXTL-Plus* was used throughout the study.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71735 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1085]

References

Exner, O. & Fiedler, P. (1987). *Collect. Czech. Chem. Commun.* **52**, 970–978.
King, J. A. Jr & Bryant, G. L. Jr (1990). *Acta Cryst.* **C46**, 1330–1334.
King, J. A. Jr & Bryant, G. L. Jr (1992). *J. Org. Chem.* **57**, 5136–5139.
O'Gorman, J. M., Shand, W. Jr & Schomaker, V. J. (1950). *J. Am. Chem. Soc.* **72**, 4222–4228.
Robinson, G. W. (1953). *J. Chem. Phys.* **21**, 1741–1745.
Sheldrick, G. M. (1988). *SHELXTL-Plus. R3m/V Crystallographic System Users Guide.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wanner, K. T., Praschak, I. & Nagel, U. (1990). *Arch. Pharm. (Weinheim)*, **323**, 335–350.

Acta Cryst. (1994). **C50**, 1108–1112

2,2′,3,3′-Tetra-*O*-acetyl-4,4′,6,6′-tetradeoxy-α,α-*xylo*-trehalose[†]

Anthony Linden

Organisch-chemisches Institut, Universität Zürich,
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

C. Kuan Lee

Department of Chemistry, Faculty of Science, National
University of Singapore, Kent Ridge, Singapore 0511

(*Received* 14 *October* 1993; *accepted* 21 *January* 1994)

Abstract

The low-temperature X-ray crystal structure of 2,2′,3,3′-tetra-*O*-acetyl-4,4′,6,6′-tetradeoxy-α,α-*xylo*-trehalose (I) (2,3-di-*O*-acetyl-4,6-dideoxy-α-D-*xylo*-hexopyranosyl 2,3-di-*O*-acetyl-4,6-dideoxy-α-D-*xylo*-hexopyranoside) is reported. The crystals were found to contain approximately 16% of 2,3-di-*O*-acetyl-6-chloro-4,6-dideoxy-α-D-*xylo*-hexopyranosyl 2,3-di-*O*-acetyl-4,6-dideoxy-α-D-*xylo*-hexopyranoside (II) as a result of incomplete hydrodechlorination of the intermediate 2,2′,3,3′-tetra-*O*-acetyl-4,4′,6,6′-tetrachloro-4,4′,6,6′-tetradeoxy-α,α-trehalose. Except for the chloro substituent, the two molecules are crystallographically identical and the structure may be refined using a disordered model with one H atom being replaced by a Cl atom in 16% of the molecules. The two hexopyranosyl residues in both molecules have $^4C_1$ conformations, with one of the residues adopting a nearly perfect chair conformation. The crystal packing places the Cl atom of (II) in a very crowded environment with a C—Cl bond length of 1.527 (7) Å and a short intermolecular Cl···C contact of 2.884 (9) Å.

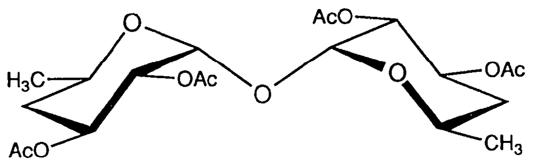
Comment

α,α-Trehalose (α-D-glucopyranosyl α-D-glucopyranoside), a natural reserve sugar, is found in many bacteria and fungi, in plants, and in the blood of most insects, where it probably plays an important role in carbohydrate metabolism (Birch, 1963). A number of trehalose analogues, particularly the aminated ones, occur naturally as antibiotically active metabolites (Arcamone & Bizioli, 1957; Umezawa, Tasuta & Muto, 1967; Uramoto, Otaka & Yonehara, 1967; Naganawa, Usui, Takita, Hamada, Maeda & Umezawa, 1974; Dolak, Castle & Laborde, 1980). There is also considerable interest in the specificity and inhibitors of the trehalases, the specific hy-

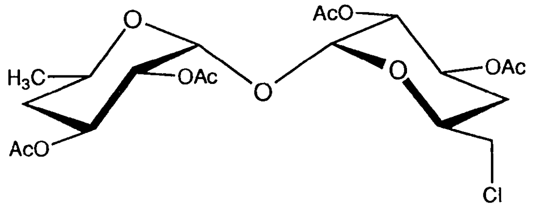
---

[†] Crystal Structures of Trehalose Derivatives, Part 5. For Part 4, see Lee & Linden (1994).

drolytic enzymes for trehalose. The disaccharide also serves as an ideal molecule for taste studies (Lee, 1973, 1987). The synthesis of the title compound (I) (Birch, Lee & Richardson, 1974) and the taste of its 2,2′,3,3′-tetrahydroxy derivative (Birch & Lee, 1974) have been published previously. We now report the X-ray crystal structure of (I).



(I)



(II)

The structure determination showed that the crystals of (I) were contaminated with (II), in which a chloromethyl, instead of a methyl, substituent exists at C(5′). The presence of (II) in the sample was a result of incomplete hydrodechlorination of the intermediate 2,2′,3,3′-tetra-*O*-acetyl-4,4′,6,6′-tetrachloro-4,4′,6,6′-tetradeoxy-α,α-trehalose, during the synthesis of (I). The two molecules occupy identical crystallographic sites in the crystal, so that the structure can be considered to be disordered, rather than having independent crystallographic sites for each type of molecule. It was necessary to define only partially occupied positions for the Cl atom and one H atom of the methyl group attached to C(5′). Refinement of the site occupation factor of the Cl atom [0.159 (3)] indicated that approximately 16% of the molecules in the crystal are compound (II). The presence of Cl atoms in the crystal was confirmed from a mass spectrum run on the same batch from which the crystal was taken. This spectrum showed that a Cl atom was present in approximately 15.6% of the molecules, in excellent agreement with the estimate from the crystal structure analysis.

A view of (I) showing the displacement ellipsoids and the atomic numbering is given in Fig. 1. In this figure, the position of the Cl atom of (II) is also shown. All other atoms of (II) are in the same positions as those of (I). Fig. 1 depicts the correct absolute configuration of the molecule as established by the synthesis of the compound.

An analysis of intermolecular contacts shows that the crystal packing is primarily arranged to accommodate molecules of (I) and not the larger molecules of (II). As a result, the Cl atom is in an extremely crowded environment. There is a very close intermolecular contact between Cl(6′) and the methyl group, C(10), of the acetyl substituent at C(3) [Cl(6′)···H(101) = 2.44, Cl(6′)···C(10) = 2.884 (9) Å]. The crystal packing, depicted in Fig. 2, shows the proximity of the Cl atom to the acetyl group with dotted lines. This close contact could be the cause of the large anisotropic displacement parameters for the atoms of the acetyl substituent (Fig. 1). These atoms are probably disordered, adopting a second distorted conformation when a molecule of (II) is adjacent to the group. Unfortunately, it was not possible to successfully refine disordered positions for the atoms of this acetyl group.

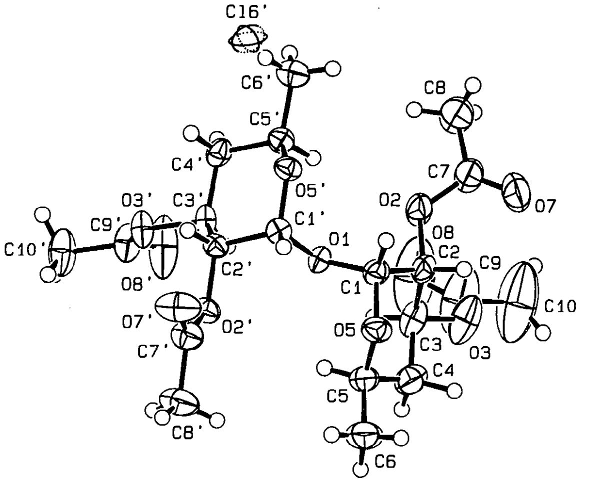


Fig. 1. View of the molecule of (I) showing the atom-labelling scheme. The position of the Cl atom of (II) has been superimposed. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by spheres of arbitrary radii.

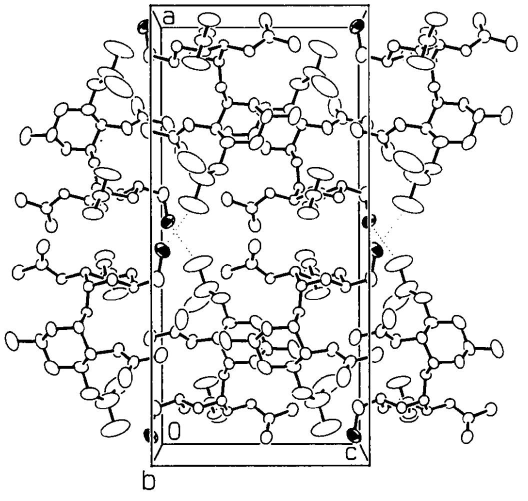


Fig. 2. The packing of molecules of (I) and (II) in the unit cell, viewed down *b*. Although only 16% of the molecules are of (II), all molecules have been drawn as those of (II) to highlight the close contacts, shown by dotted lines, between the Cl atoms (shaded) and neighbouring acetyl groups.

The crowding around the Cl atom is further evidenced by the C(6′)—Cl(6′) bond [1.527 (7) Å], which is approximately 0.24 Å shorter than normal C—Cl bonds [1.77 Å (Dunitz, 1979)]. In the related trehalose derivative, 2,2′,3,3′-tetra-*O*-acetyl-6,6′-dichloro-4,4′,6,6′-tetradeoxy-α,α-trehalose (Lee, Koh, Xu & Linden, 1994), the mean C—Cl distance is 1.78 (3) Å. There is no evidence, either in the displacement parameters or the residual electron density map, to suggest that the positions of C(6′) or C(5′) are distorted in molecules of (II) in order to allow a longer C—Cl bond, although the low proportion of (II) in the structure may make such distortions difficult to detect. It is possible that the position of the Cl atom is a result of overlap with the C—H bond; however, if the true C(6′)—Cl(6′) bond length was much closer to the expected distance, the Cl(6′)···C(10) contact distance would, necessarily, be significantly shorter than 2.88 Å, which does not alleviate the problem of crowding of the Cl atom.

A second data collection from a different crystal revealed the same features in the structure and confirmed that the unusual feature in the structure is not the result of an imperfect crystal.

Apart from the effects of disorder, there are no unusual geometrical features in the structure of (I). As observed with α,α-trehalose (Brown, Rohrer, Berking, Beevers, Gould & Simpson, 1972; Taga, Senma & Osaki, 1972; Jeffrey & Nanni, 1985) and its derivatives (Lee & Koh, 1994; Lee, Koh, Xu & Linden, 1994), the two hexopyranosyl residues in (I) are not exactly related by a twofold axis of symmetry through O(1). There are significant differences in the relative conformations of the acetyl groups and the torsion angles about the C(1)—O(1) bond are also different from those about the C(1′)—O(1) bond (Table 3).

The conformations of the hexopyranosyl rings are ${}^4C_1$. Ring *A*, with puckering parameters (Cremer & Pople, 1975) $Q = 0.576$ Å, $\theta = 0.51°$, $\varphi_2 = 358.3°$, $q_2 = 0.005$ Å, $q_3 = 0.576$ Å, is clearly a nearly perfect chair. Ring *B* (primed atoms), with $Q = 0.577$ Å, $\theta = 2.59°$, $\varphi_2 = 98.46°$, $q_2 = 0.026$ Å, $q_3 = 0.577$ Å, is slightly distorted towards the ${}^2H_1$ conformation. The pyranosyl residues are more symmetrically oriented about the glycosidic O atom than in α,α-trehalose dihydrate, as shown by the two glycosidic torsion angles [83.0 (3) and 89.0 (3)° for (I) *versus* 78.8 and 61.7° for α,α-trehalose dihydrate (Brown, Rohrer, Berking, Beevers, Gould & Simpson, 1972)].

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	$U_{\rm eq}$
O(1)	0.67109 (9)	0.2646 (2)	0.6817 (2)	0.0328 (7)
O(2)	0.7529 (1)	0.1725 (3)	0.8364 (2)	0.055 (1)
O(3)	0.8530 (1)	0.2629 (4)	0.6955 (3)	0.076 (1)
O(5)	0.7060 (1)	0.1203 (3)	0.5291 (2)	0.0416 (8)
O(7)	0.8086 (2)	−0.0125 (5)	0.8802 (3)	0.103 (2)
O(8)	0.8417 (2)	0.4443 (5)	0.8159 (5)	0.172 (3)
C(1)	0.7022 (2)	0.1398 (4)	0.6541 (3)	0.036 (1)
C(2)	0.7610 (2)	0.1499 (4)	0.7094 (3)	0.042 (1)
C(3)	0.7942 (2)	0.2714 (5)	0.6532 (4)	0.051 (1)
C(4)	0.7950 (2)	0.2517 (5)	0.5177 (4)	0.055 (2)
C(5)	0.7355 (2)	0.2386 (5)	0.4693 (3)	0.049 (1)
C(6)	0.7338 (2)	0.2023 (5)	0.3361 (4)	0.069 (2)
C(7)	0.7784 (2)	0.0812 (5)	0.9126 (4)	0.060 (2)
C(8)	0.7635 (2)	0.1131 (6)	1.0386 (4)	0.083 (2)
C(9)	0.8723 (3)	0.3568 (7)	0.7701 (7)	0.127 (3)
C(10)	0.9329 (3)	0.3303 (8)	0.8101 (7)	0.169 (4)
O(2′)	0.59697 (9)	0.4340 (2)	0.5484 (2)	0.0367 (7)
O(3′)	0.56503 (9)	0.6202 (2)	0.7368 (3)	0.0430 (8)
O(5′)	0.59723 (9)	0.1946 (2)	0.8072 (2)	0.0346 (7)
O(7′)	0.5243 (1)	0.3087 (3)	0.4730 (2)	0.066 (1)
O(8′)	0.6366 (1)	0.7629 (3)	0.7834 (4)	0.097 (2)
C(1′)	0.6119 (1)	0.2439 (4)	0.6930 (3)	0.031 (1)
C(2′)	0.5821 (2)	0.3841 (4)	0.6660 (3)	0.031 (1)
C(3′)	0.5999 (2)	0.4935 (3)	0.7571 (3)	0.034 (1)
C(4′)	0.5869 (2)	0.4362 (4)	0.8826 (3)	0.038 (1)
C(5′)	0.6144 (2)	0.2918 (4)	0.9024 (3)	0.037 (1)
C(6′)	0.5965 (2)	0.2227 (5)	1.0192 (3)	0.059 (2)
C(7′)	0.5640 (2)	0.3868 (4)	0.4580 (4)	0.045 (1)
C(8′)	0.5828 (2)	0.4439 (5)	0.3400 (4)	0.064 (2)
C(9′)	0.5888 (2)	0.7482 (4)	0.7518 (4)	0.049 (1)
C(10′)	0.5484 (2)	0.8633 (4)	0.7223 (5)	0.067 (2)
Cl(6′)†	0.5325 (3)	0.2067 (9)	1.0411 (6)	0.069 (3)

† Site occupancy factor = 0.159 (3).

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

O(1)—C(1)	1.415 (4)	O(1)—C(1′)	1.408 (4)
O(2)—C(2)	1.441 (4)	O(2′)—C(2′)	1.433 (4)
O(2)—C(7)	1.347 (5)	O(2′)—C(7′)	1.345 (4)
O(3)—C(3)	1.458 (5)	O(3′)—C(3′)	1.462 (4)
O(3)—C(9)	1.293 (6)	O(3′)—C(9′)	1.335 (4)
O(5)—C(1)	1.406 (4)	O(5′)—C(1′)	1.396 (4)
O(5)—C(5)	1.467 (4)	O(5′)—C(5′)	1.455 (4)
O(7)—C(7)	1.185 (5)	O(7′)—C(7′)	1.197 (4)
O(8)—C(9)	1.205 (6)	O(8′)—C(9′)	1.183 (4)
C(1)—C(2)	1.512 (5)	C(1′)—C(2′)	1.520 (5)
C(2)—C(3)	1.516 (5)	C(2′)—C(3′)	1.503 (5)
C(3)—C(4)	1.521 (6)	C(3′)—C(4′)	1.528 (5)
C(4)—C(5)	1.501 (6)	C(4′)—C(5′)	1.518 (5)
C(5)—C(6)	1.522 (5)	C(5′)—C(6′)	1.513 (5)
C(7)—C(8)	1.476 (6)	C(7′)—C(8′)	1.486 (5)
C(9)—C(10)	1.510 (8)	C(9′)—C(10′)	1.474 (5)
Cl(6′)—C(6′)	1.527 (7)		
C(1)—O(1)—C(1′)	114.5 (3)	Cl(6′)—C(6′)—C(5′)	116.9 (4)
C(2)—O(2)—C(7)	117.7 (3)	C(2′)—O(2′)—C(7′)	115.8 (3)
C(3)—O(3)—C(9)	120.0 (4)	C(3′)—O(3′)—C(9′)	118.7 (2)
C(1)—O(5)—C(5)	112.3 (3)	C(1′)—O(5′)—C(5′)	112.8 (2)
O(1)—C(1)—O(5)	110.8 (3)	O(1)—C(1′)—O(5′)	111.7 (3)
O(1)—C(1)—C(2)	109.3 (3)	O(1)—C(1′)—C(2′)	108.4 (3)
O(5)—C(1)—C(2)	110.7 (3)	O(5′)—C(1′)—C(2′)	110.7 (3)
O(2)—C(2)—C(1)	106.7 (3)	O(2′)—C(2′)—C(1′)	110.6 (3)
O(2)—C(2)—C(3)	111.2 (3)	O(2′)—C(2′)—C(3′)	109.0 (3)
C(1)—C(2)—C(3)	110.3 (3)	C(1′)—C(2′)—C(3′)	109.3 (3)
O(3)—C(3)—C(2)	108.1 (4)	O(3′)—C(3′)—C(2′)	107.2 (3)
O(3)—C(3)—C(4)	107.5 (3)	O(3′)—C(3′)—C(4′)	108.4 (3)
C(2)—C(3)—C(4)	108.9 (4)	C(2′)—C(3′)—C(4′)	108.7 (3)
C(3)—C(4)—C(5)	110.7 (3)	C(3′)—C(4′)—C(5′)	111.2 (3)
O(5)—C(5)—C(4)	109.7 (3)	O(5′)—C(5′)—C(4′)	109.7 (3)
O(5)—C(5)—C(6)	105.1 (3)	O(5′)—C(5′)—C(6′)	106.2 (3)
C(4)—C(5)—C(6)	113.0 (4)	C(4′)—C(5′)—C(6′)	112.9 (3)
O(2)—C(7)—O(7)	123.1 (4)	O(2′)—C(7′)—O(7′)	123.1 (4)
O(2)—C(7)—C(8)	111.4 (4)	O(2′)—C(7′)—C(8′)	111.8 (3)
O(7)—C(7)—C(8)	125.5 (4)	O(7′)—C(7′)—C(8′)	125.1 (4)
O(3)—C(9)—O(8)	121.9 (5)	O(3′)—C(9′)—O(8′)	122.5 (4)
O(3)—C(9)—C(10)	114.0 (6)	O(3′)—C(9′)—C(10′)	111.4 (3)
O(8)—C(9)—C(10)	123.2 (6)	O(8′)—C(9′)—C(10′)	126.1 (4)

Table 3. *Selected torsion angles* (°)

Within the pyranosyl rings			
C(1)—C(2)—C(3)—C(4)	−54.7 (4)	C(1′)—C(2′)—C(3′)—C(4′)	−56.0 (4)
C(1)—O(5)—C(5)—C(4)	60.1 (4)	C(1′)—O(5′)—C(5′)—C(4′)	58.5 (4)
C(2)—C(1)—O(5)—C(5)	−60.5 (4)	C(2′)—C(1′)—O(5′)—C(5′)	−61.7 (3)
C(2)—C(3)—C(4)—C(5)	55.1 (5)	C(2′)—C(3′)—C(4′)—C(5′)	54.7 (4)
O(5)—C(1)—C(2)—C(3)	58.0 (4)	O(5′)—C(1′)—C(2′)—C(3′)	60.3 (3)
O(5)—C(5)—C(4)—C(3)	−56.7 (5)	O(5′)—C(5′)—C(4′)—C(3′)	−54.4 (4)
Outside the pyranosyl rings			
C(1)—O(1)—C(1′)—C(2′)	−154.7 (3)	C(1′)—O(1)—C(1)—C(2)	−148.7 (3)
C(1)—O(1)—C(1′)—O(5′)	83.0 (3)	C(1′)—O(1)—C(1)—O(5)	89.0 (3)
C(1)—C(2)—O(2)—C(7)	125.2 (4)	C(1′)—C(2′)—O(2′)—C(7′)	88.2 (3)
C(1)—O(5)—C(5)—C(6)	−178.2 (3)	C(1′)—O(5′)—C(5′)—C(6′)	−179.2 (3)
C(2)—C(3)—O(3)—C(9)	−109.3 (6)	C(2′)—C(3′)—O(3′)—C(9′)	−143.6 (3)
C(3)—C(4)—C(5)—C(6)	−173.6 (4)	C(3′)—C(4′)—C(5′)—C(6′)	−172.7 (3)
O(1)—C(1)—O(5)—C(5)	60.9 (4)	O(1)—C(1′)—O(5′)—C(5′)	59.2 (3)
O(1)—C(1)—C(2)—O(2)	56.6 (4)	O(1)—C(1′)—C(2′)—O(2′)	57.5 (3)
O(1)—C(1)—C(2)—C(3)	−64.3 (4)	O(1)—C(1′)—C(2′)—C(3′)	−62.5 (4)
O(2)—C(2)—C(3)—O(3)	70.6 (4)	O(2′)—C(2′)—C(3′)—O(3′)	66.0 (4)
O(2)—C(2)—C(3)—C(4)	−172.9 (3)	O(2′)—C(2′)—C(3′)—C(4′)	−177.0 (3)
O(3)—C(3)—C(4)—C(5)	172.0 (3)	O(3′)—C(3′)—C(4′)—C(5′)	170.9 (3)
O(7)—C(7)—O(2)—C(2)	2.8 (7)	O(7′)—C(7′)—O(2′)—C(2′)	0.4 (5)
O(8)—C(9)—O(3)—C(3)	7 (1)	O(8′)—C(9′)—O(3′)—C(3′)	−1.6 (6)
Cl(6′)—C(6′)—C(5′)—O(5′)	−66.3 (5)	Cl(6′)—C(6′)—C(5′)—C(4′)	54.0 (6)

Experimental

Synthesis was as reported by Birch, Lee & Richardson (1974). Suitable crystals were obtained form an ethanol solution.

Crystal data

$(C_{20}H_{30}O_{11})_{0.841}$.-
$(C_{20}H_{29}ClO_{11})_{0.159}$
$M_r = 451.92$
Orthorhombic
$P2_12_12$
$a = 23.446$ (3) Å
$b = 9.390$ (2) Å
$c = 11.130$ (2) Å
$V = 2450.3$ (7) Å^3
$Z = 4$
$D_x = 1.225$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 24 reflections
$\theta = 11$-$18°$
$\mu = 0.110$ mm^{-1}
$T = 173$ (1) K
Prism
0.43 × 0.35 × 0.33 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.57$, $T_{\max} = 1.14$
4655 measured reflections
4533 independent reflections
3016 observed reflections
$[I > 3\sigma(I)]$

$R_{\rm int} = 0.023$
$\theta_{\max} = 30°$
$h = -1 \rightarrow 32$
$k = -1 \rightarrow 13$
$l = 0 \rightarrow 15$
3 standard reflections monitored every 150 reflections
intensity variation: insignificant

Refinement

Refinement on F
$R = 0.0506$
$wR = 0.0477$
$S = 2.688$
3016 reflections

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

338 parameters
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$
$(\Delta/\sigma)_{\max} = 0.0003$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}

Absolute configuration: assigned to agree with the known chirality at C(5) as established by the synthesis of the compound

During the refinement the behaviour of some of the acetyl groups, especially the group bonded to C(3), indicated that they are slightly disordered; however, attempts to refine a disordered model did not produce acceptable results. An ordered model was employed for the final refinement and the enlarged displacement ellipsoids for some of the atoms of these groups reflect the 'smeared-out' electron density resulting from the disorder. The H atoms of the hexopyranosyl rings were located from a difference electron density map and refined isotropically. All of the remaining H atoms were placed in geometrically calculated positions and were assigned fixed isotropic displacement parameters with a value of 1.2 × $U_{\rm eq}$ of the parent C atom.

After assigning the atoms corresponding to the expected compound, (I), a significant peak of electron density (1.8 e Å^{-3}) was found 1.46 Å from the Me group bonded to C(5′). It was initially unclear which element this peak represented, since the C(6′)—*X* bond length suggested that it might be an O atom. Subsequently, a mass spectrum indicated the presence of a Cl atom in approximately 15.6% of the molecules and since (II) is a synthetic precursor of (I), the presence of an O atom was ruled out. The peak was therefore assigned to a Cl atom and the site-occupancy factor was allowed to refine. Anisotropic refinement of the Cl atom produced satisfactory displacement parameters and the site occupancy factor refined to 0.159 (3). Thus 16% of the molecules are the chloro derivative, (II), which is in excellent agreement with the estimate from the mass spectrum.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: direct methods in *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

One of us (CKL) wishes to thank the National University of Singapore for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Arcamone, F. & Bizioli, F. (1957). *Gazzetta*, **87**, 896-902.
Birch, G. G. (1963). *Adv. Carbohydr. Chem.* **18**, 201-225.
Birch, G. G. & Lee, C. K. (1974). *J. Food Sci.* **39**, 947-949.
Birch, G. G., Lee, C. K. & Richardson, A. C. (1974). *Carbohydr. Res.* **36**, 97-109.
Brown, G. M., Rohrer, D. C., Berking, B., Beevers, C. A., Gould, R. O. & Simpson, R. (1972). *Acta Cryst.* **B28**, 3145-3158.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354-1358.
Dolak, L. A., Castle, T. M. & Laborde, A. L. (1980). *J. Antibiot.* **33**, 690-694.
Dunitz, J. D. (1979). *X-ray Analysis and the Structure of Organic Molecules*, p. 338. Ithaca: Cornell Univ. Press.
Jeffrey, G. A. & Nanni, R. (1985). *Carbohydr. Res.* **137**, 21-30.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lee, C. K. (1973). PhD thesis, Univ. of Reading, England.
Lee, C. K. (1987). *Adv. Carbohydr. Chem. Biochem.* **45**, 199-351.
Lee, C. K. & Koh, L. L. (1994). *Carbohydr. Res.* **254**, 281-287.
Lee, C. K., Koh, L. L., Xu, Y. & Linden, A. (1994). *Acta Cryst*, **C50**. 915-919.
Lee, C. K. & Linden, A. (1994). *J. Carbohydr. Chem.* In the press.
Molecular Structure Corporation (1989). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1991). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Naganawa, H., Usui, N., Takita, T., Hamada, M., Maeda, K. & Umezawa, H. (1974). *J. Antibiot.* **27**, 145-146.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467-473.
Taga, T., Senma, M. & Osaki, K. (1972). *Acta Cryst.* **B28**, 3258-3263.
Umezawa, S., Tasuta, K. & Muto, R. (1967). *J. Antibiot. Ser. A*. **20**, 388-389.
Uramoto, M., Otaka, N. & Yonehara, H. (1967). *J. Antibiot. Ser. A*, **20**, 236.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158-166.

Acta Cryst. (1994). **C50**, 1112–1114

Octabutyltetrasila[2.2]terthiophenophane

JAN K. HERREMA AND JURJEN WILDEMAN

Laboratory of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

FRÉ VAN BOLHUIS

Crystal Structure Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

GEORGES HADZIIOANNOU

Laboratory of Polymer Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

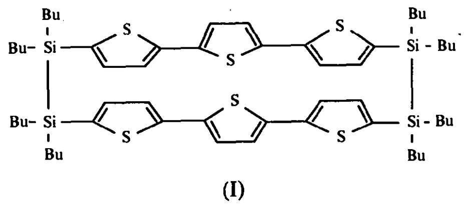
(*Received* 3 *June* 1993; *accepted* 19 *January* 1994)

Abstract

The title compound, 1,1,1′,1′,2,2,2′,2′-octabutyl-1,1′,2,2′-tetrasila[2.2](9,20)α,α'-terthiophenophane (10,10,11,11,24,24,25,25-octa-*n*-butyl-29,30,31,32,33,34-hexathia-10,11,24,25-tetrasilaheptacyclo[24.2.1.$1^{2,5}$.$1^{6,9}$.$1^{12,15}$.$1^{16,19}$.$1^{20,23}$]tetratriaconta-2,4,6,8,12,14,16,18,20,22,26,28-dodecaene, $C_{56}H_{84}S_6Si_4$) provides the first example of the crystal structure of a [2.2]thiophenophane bridged by silanes. The molecule is centrosymmetric and the thiophene rings are nearly planar.

Comment

As part of our studies of the synthesis and structures of poly(silanylene)thiophenes, we recently reported the isolation of cyclic compounds formed as by-products during the synthesis of the polymers (Wildeman, Herrema, Hadziioannou & Schomaker, 1991). These cyclic compounds, consisting of $\sigma-\pi$ conjugations, are of interest because of their special electronic and chemical properties. A few X-ray data on paracyclophanes are given in the literature and, although the photoelectron spectrum of octamethyltetrasila[2.2](2,5)thiophenophane has been reported (Gleiter, Schäfer, Krennrich & Sakurai, 1988), no crystal structure of a thiophenophane bridged by polysilanes has been reported until now.



(I)

Acta Crystallographica Section C
ISSN 0108-2701 ©1994