Table 7. *Comparison of geometrical data in some multi oxacyclohexanes*

(For explanation of the symbols see Fig. 1.)

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	(*g*)
α	104·8	104·8	104·9	104·8	105·6	106·9	104·9
β	119·9	119·4	119·3	119·3	120·0	120·0	119·9
d_1	1·473	1·481	1·478	1·478	1·495	1·487	1·480
d_2	1·455	1·450	1·464	1·465	1·458	1·470	1·463
d_3	1·435	1·435	1·442	1·435	1·439	1·437	1·447

(*a*) *anti*-2,3;4,5-*syn*-7,8;9,10-Tetraepoxy-12-oxa[4.4.3]propellane (Kaftory, present work).
(*b*) *anti*-2,3;4,5-Diepoxy-12-oxa[4.4.3]propella-7,9-diene (Kaftory, present work).
(*c*) *syn*-2,3;4,5-Diepoxy-12-oxa[4.4.3]propellane-11,13-dione (Kaftory, 1979). [The values given here are the mean values of form (*A*) and form (*B*).]
(*d*) *syn*-2,3;4,5-Diepoxy-12-methyl-12-aza[4.4.3]propellane-11,13-dione (Kaftory, 1978).
(*e*) *syn,syn,syn,syn*-1,2;3,4;5,6;7,8-*anti*-9,10-Naphthalene pentoxide (Vogel, Breuer, Sommerfeld, Davis & Liu, 1977). (The geometrical parameters involving the central ring were eliminated.)
(*f*) *cis*-Trioxatris-σ-homobenzene (Littke & Drück, 1974).
(*g*) 9-Cyano-*anti*-dioxatris-σ-homobenzene (Kabuto, Yagihara, Asao & Kitahara, 1973).

There is good agreement between the dihedral angles (α) (104·8 ~ 106·9°). (In *e*, *f* and *g* the cyclohexane ring is planar and the dihedral angle is defined by the angle between this plane and the plane of the epoxy ring; in *a*, *b*, *c* and *d* it is the angle between the epoxy ring plane and the plane through the two C atoms bonded to the O atom and the next bonded atoms on both sides.)

The shortening of the C—C single-bond distances (d_1 = 1·473–1·495; d_2 = 1·450–1·470 Å) corresponds to an sp^2–sp^2 single bond, although the C atoms are in sp^3 hybridization, and is an indication for multi-conjugated interactions which occur between three-membered rings, as assumed between cyclopropane rings and double bonds. The values observed for the angle β (119·3–120·0°) are similar to those observed in conjugated systems and suggest that the ring is an intermediate of cyclohexane with sp^3 C atoms and benzene with sp^2 C atoms.

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The Crystal and Molecular Structure of 6,6′-Dibromo-6,6′-dideoxy-α,α-trehalose Hexaacetate Chloroform Adduct, $C_{24}H_{32}Br_2O_{15}.CHCl_3$

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Abstract

The crystal structure of $C_{24}H_{32}Br_2O_{15}.CHCl_3$ has been solved by direct methods from 3658 independent reflections and refined by a least-squares block-diagonal approximation to a final R value of 0·084. The crystal data are: a = 11·532 (7), b = 18·340 (8), c = 16·810 (10) Å, β = 91·35 (10)°, space group $P2_1$. There are two molecules of each 6,6′-dibromo-trehalose hexaacetate and chloroform per asymmetric

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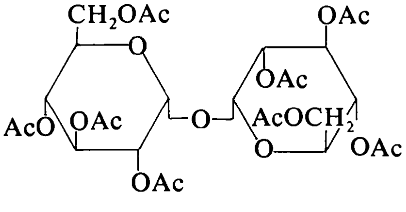
unit. Dibromotrehalose hexaacetate has approximate 2 symmetry; its conformation is very similar to that of the unsubstituted trehalose molecule.

Introduction

α,α-Trehalose, or α-D-glucopyranosyl α-D-glucopyranoside, is a disaccharide stored for food in fungi. It is also found in algae, lichens and bacteria and it constitutes the blood sugar of many insects [see for example Defaye, Driguez, Henrissat, Gelas & Bar-Guilloux (1978), and references cited therein]. The molecule of trehalose, which has been extensively studied by X-ray diffraction methods (Brown, Rohrer, Berking, Beevers, Gould & Simpson, 1972; Cook & Bugg, 1973), has two interesting structural features. First of all, the two glycosyl units are in a symmetrical disposition around the glycosidic oxygen. In fact, in α,α-trehalose calcium bromide monohydrate (Cook & Bugg, 1973) the two glycosyl units are crystallographically related by a twofold axis of rotation passing through the central O atom, while the molecule has approximate C_2 (2) symmetry in the case of α,α-trehalose dihydrate (Brown *et al.*, 1972). The second interesting feature is the α-linkage which has a strong bearing on its enzymatic behaviour.

Among the chemical modifications of trehalose, it has been established that 6-deoxy-α,α-trehalose, but not the 6,6′-dideoxy analogue, is a substrate for trehalases (Guilloux, Defaye, Bell & Horton, 1971).

The determination of the crystal structure of 6,6′-dibromo-6,6′-dideoxy-α,α-trehalose hexaacetate is part of a study in which we intended to correlate the effect of substitution with general conformational properties of the molecule in the crystalline state. In order to detect some eventual differences, three monosubstituted trehalose derivatives of (I) were also investigated, namely 6-monochlorotrehalose heptaacetate, 6-monobromotrehalose heptaacetate and 6-monodeoxytrehalose heptaacetate. However, for reasons given in the experimental section this part of the undertaking had to be abandoned.



Experimental

The various substituted trehalose compounds mentioned in this study were synthesized by Hanessian & Lavallée (1973). The crystal data for the two monosubstituted trehalose acetates, 6-monochlorotrehalose heptaacetate and 6-monodeoxytrehalose heptaacetate, both crystallized from chloroform solutions, are listed in Table 1. There are two 6-monochlorotrehalose heptaacetate molecules per asymmetric unit as well as a number of chloroform molecules. The crystals decompose very easily in air even when sealed in a glass capillary and give only a limited number of reflections. Therefore we do not expect to obtain accurate data and no further work is contemplated with this compound. The same comments also apply to 6-monodeoxytrehalose heptaacetate.

Good needle-shaped crystals of dibromotrehalose hexaacetate were obtained by vapour diffusion of Et_2O into a solution of the compound in chloroform. The originally colourless crystals became opaque upon standing in air and exposure to X-rays. To retard this process, the mounted crystal was coated by dipping it into a solution of polystyrene in $CHCl_3/CCl_4$. The crystal used in this work was a six-sided prism whose dimensions, measured perpendicular to [100], [10$\bar{1}$], [102] and [010], were 0·10 × 0·20 × 0·25 × 0·50 mm respectively. Preliminary photography revealed $2/m$ diffraction symmetry and the systematic absences were for $0k0$ when $k = 2n + 1$. The unit-cell dimensions were obtained as part of the alignment process on the Picker FACS-1 diffractometer. These and other crystal data are given in Table 1. Because of the high solubility of these crystals in most organic solvents and the apparent reactivity of suitable inorganic solutions some difficulty was experienced in obtaining satisfactory density values. They ranged from 1·49 Mg m^{-3} (in KI solution) to 1·57 Mg m^{-3} (in $ZnCl_2$ solution or a $CHBr_3$/cyclohexane mixture). Because the latter figure was *a priori* believed to be more reliable, it is the one adopted here. The calculated density for four molecules of dibromotrehalose hexaacetate alone in the unit cell is 1·35 Mg m^{-3}. This discrepancy and the fact that our crystals had the same appearance and melting point as those grown by Hanessian & Lavallée (1973) from

Table 1. *Crystal data*

6,6′-Dibromotrehalose hexaacetate chloroform
$C_{24}H_{32}Br_2O_{15}.CHCl_3$, FW = 730·58 + 119·39, $F(000) = 1696$.
Monoclinic, space group $P2_1$
$a = 11{\cdot}532\,(7)$, $b = 18{\cdot}340\,(8)$, $c = 16{\cdot}810\,(10)$ Å, $\beta = 91{\cdot}35\,(10)°$
$V = 3554{\cdot}3$ Å^3, $d_o = 1{\cdot}57$, $d_c = 1{\cdot}569$ Mg m^{-3}, $Z = 4$
$\lambda(\mathrm{Cu}\ K\alpha_1) = 1{\cdot}540562$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 5{\cdot}342$ mm^{-1}

6-Monochlorotrehalose heptaacetate
$C_{26}H_{35}ClO_{17}$, FW = 654·99
Orthorhombic, space group $P2_122_1$
$a = 16{\cdot}46$, $b = 37{\cdot}20$, $c = 11{\cdot}74$ Å, $V = 7206$ Å^3
$d_o = 1{\cdot}38$, $d_c = 1{\cdot}208$ Mg m^{-3}, $Z = 8$

6-Monodeoxytrehalose heptaacetate
$C_{27}H_{38}O_{17}$, FW = 634·58
Hexagonal, space group $P6_1$ or $P6_5$
$a = b = 15{\cdot}55$, $c = 47{\cdot}11$ Å, $V = 9862$ Å^3
$d_c = 1{\cdot}283$ Mg m^{-3}, $Z = 12$

absolute ethanol caused some concern until the crystal structure was fully resolved.

The data collection was performed by the θ–2θ technique over a basic peak width of 1·40° (2θ) at a scan rate of 2° (2θ) min^{-1} using graphite-monochromatized Cu $K\alpha$ radiation. Background counts of 20 s were taken at each end of the scan range. The intensities of three reference reflections, monitored every 50 reflections, decreased by 40% over the duration of the intensity measurements. This decrease was taken into account during the data reduction which was performed using the programs[†] of Ahmed, Hall, Pippy & Huber (1973). Absorption corrections were applied using the method of Gaussian integration. The transmission factor ranged from 0·60 to 0·85. To correct for secondary extinction, the quantity $\mathrm{d}A^*/\mathrm{d}\mu$ was evaluated for all reflections (Åsbrink & Werner, 1966). Of the 6562 reflections within the hkl and $hk\bar{l}$ octants limited by $2\theta < 125°$, only 3658 reflections were found to have net intensities $>2\cdot5\sigma(I)$, where $\sigma(I)$ was calculated by a relation described by Brisse & Pérez (1976). The scattering factors for the non-hydrogen atoms were derived from the set of coefficients of Cromer & Mann (1968). The Br and Cl curves were corrected for anomalous dispersion using the values given by Cromer & Liberman (1970). The hydrogen scattering curve was that of Stewart, Davidson & Simpson (1965).

Structure determination and refinement

A set of normalized structure factors was obtained after isotropic temperature factor correction, but because of the uncertainty of this compound's density, one extra Br atom per substituted trehalose molecule was assumed. All E's down to 1·80 were used in the *MULTAN* procedure. Among the 32 sets examined six of them had R Karle values around 0·24. The E map calculated using the set with the highest figure of merit among those six sets contained peaks corresponding to three Br and 32 lighter atoms. This initial model was expanded to the full 90 non-hydrogen atoms in the asymmetric unit by a succession of structure factor Fourier syntheses calculations. It was during this process that the chloroform molecules were revealed so that the asymmetric unit does in fact contain two molecules of dibromotrehalose hexaacetate and two molecules of chloroform. When the density is calculated with all these molecules, it agrees very well with the experimental value measured in $ZnCl_2$ solution. The full-matrix least-squares refinement of all non-hydrogen atoms with isotropic temperature factors converged to $R = \sum \Delta F/\sum F_o = 0\cdot145$. The ring H atoms were then included and refined with fixed isotropic temperature factors while for all other atoms the temperature factors were now refined anisotropically using unit weights. Because of the large number of atoms in the asymmetric unit, only half of the parameters could be refined at a time, even with the use of the block-diagonal approximation. At the end of the refinement when $R = 0\cdot084$* the secondary-extinction coefficient was $g = 0\cdot71\,(14) \times 10^4$ and the final difference electron density map showed some residual peaks of about 0·8 e Å^{-3} in the neighbourhood of the Br atoms and the chloroform molecules. It should be noted that the 32 methyl H atoms were not found and therefore were not included in the structure factor calculation.

Results and discussion

The positional parameters and their standard deviations are presented in Table 2. As mentioned earlier the structure consists of two molecules of 6,6′-dibromotrehalose hexaacetate and two molecules of chloroform per asymmetric unit. An *ORTEP* view (Fig. 1) allows comparison of the two molecules.

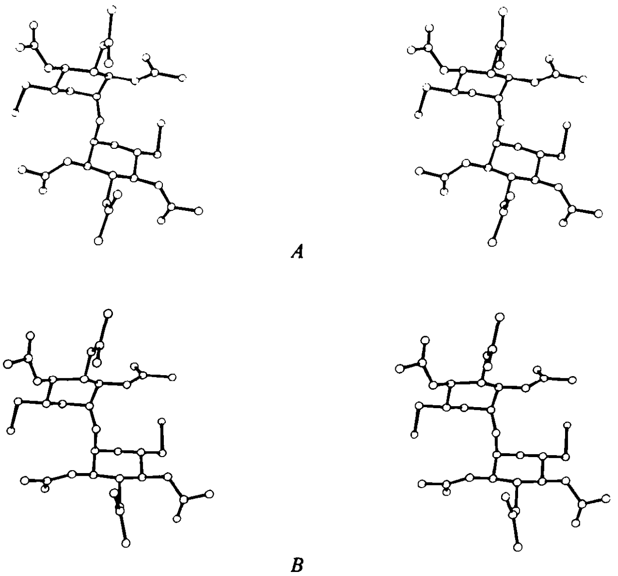


Fig. 1. *ORTEP* views (Johnson, 1965) of the two 6,6′-bromotrehalose hexaacetate molecules in the asymmetric unit.

[†] The computer programs used were locally modified versions of the following: *NRC*-2: data reduction; *NRC*-3: absorption correction (Ahmed *et al.*, 1973); *FORDAP*: Fourier and Patterson maps (A. Zalkin); *NUCLS*: least-squares refinement (R. J. Doedens & J. A. Ibers) with block-diagonal approximation option introduced by J. Sygusch; *MULTAN*: multisolution program (Germain, Main & Woolfson, 1971); *ORTEP*: stereo drawings (Johnson, 1965).

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34625 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional coordinates and their e.s.d.'s* ($\times 10^4$, *for* H $\times$ 10^3), U_{eq} ($\times 10^4$ *for* Br, $\times 10^3$ *for* Cl, O *and* C) *and* U_{iso} ($\times 10^3$ *for* H)

	Molecule *A*				Molecule *B*			
	x	y	z	U_{eq}/U_{iso} (Å^2)	x	y	z	U_{eq}/U_{iso} (Å^2)
Br(6)	4125 (3)	0	6677 (1)	1166	7718 (2)	−546 (1)	12225 (1)	797
Br(6′)	2774 (3)	−286 (1)	1958 (1)	972	8841 (3)	−215 (2)	7438 (1)	1004
C(1)	4706 (16)	469 (9)	4152 (8)	57	9313 (17)	330 (9)	10062 (8)	44
C(2)	5477 (18)	1037 (9)	3826 (9)	56	10115 (18)	1013 (8)	9994 (9)	36
O(2)	5754 (11)	893 (6)	3047 (6)	65	10844 (11)	971 (6)	9353 (6)	50
C*A*(2)	5175 (20)	1161 (11)	2404 (11)	80	10478 (19)	1173 (9)	8621 (8)	71
O*A*(2)	4357 (13)	1624 (7)	2590 (7)	88	9463 (14)	1433 (7)	8528 (6)	71
C*M*(2)	5552 (20)	997 (12)	1594 (8)	81	11335 (21)	1121 (11)	7975 (10)	94
C(3)	6607 (18)	1115 (9)	4327 (9)	55	10805 (18)	1088 (9)	10770 (10)	59
O(3)	7164 (12)	1799 (6)	4076 (6)	59	11359 (12)	1816 (6)	10744 (7)	60
C*A*(3)	8281 (24)	1803 (11)	3997 (11)	84	12533 (19)	1857 (9)	10689 (10)	73
O*A*(3)	8942 (14)	1237 (8)	4040 (9)	96	13140 (13)	1344 (7)	10516 (8)	93
C*M*(3)	8789 (24)	2591 (12)	3944 (11)	96	12936 (22)	2640 (10)	10848 (12)	90
C(4)	6277 (18)	1212 (10)	5177 (9)	52	10125 (16)	1063 (8)	11461 (7)	46
O(4)	7397 (13)	1171 (6)	5661 (6)	70	10850 (12)	1021 (6)	12201 (7)	57
C*A*(4)	7844 (19)	1741 (10)	6074 (10)	73	11038 (19)	1626 (10)	12638 (9)	61
O*A*(4)	7263 (15)	2297 (8)	6088 (8)	103	10643 (14)	2194 (7)	12490 (6)	67
C*M*(4)	8923 (23)	1615 (12)	6451 (13)	101	11769 (19)	1419 (13)	13355 (11)	70
C(5)	5502 (18)	622 (9)	5465 (9)	57	9327 (16)	361 (9)	11473 (7)	34
O(5)	4501 (12)	624 (6)	4976 (6)	58	8707 (10)	358 (6)	10781 (6)	43
C(6)	5215 (22)	764 (10)	6337 (10)	67	8599 (20)	376 (11)	12209 (11)	73
O(1)	5263 (11)	−218 (6)	4087 (5)	48	10075 (11)	−287 (5)	10066 (6)	37
C(1′)	4454 (17)	−821 (8)	4226 (8)	41	9466 (17)	−939 (9)	9867 (9)	34
C(2′)	5183 (17)	−1500 (9)	4456 (8)	46	10149 (19)	−1592 (9)	10154 (10)	60
O(2′)	5946 (11)	−1348 (6)	5094 (6)	54	10494 (12)	−1535 (6)	10962 (6)	55
C*A*(2′)	5903 (18)	−1744 (10)	5752 (10)	86	9777 (18)	−1861 (9)	11495 (8)	64
O*A*(2′)	5158 (21)	−2190 (11)	5816 (8)	166	8898 (13)	−2169 (7)	11250 (7)	66
C*M*(2′)	6679 (24)	−1546 (11)	6430 (9)	100	10256 (23)	−1781 (13)	12341 (11)	77
C(3′)	5855 (18)	−1723 (9)	3737 (9)	50	11257 (19)	−1663 (9)	9695 (9)	49
O(3′)	6330 (12)	−2468 (6)	3953 (6)	55	11752 (12)	−2389 (6)	9898 (6)	53
C*A*(3′)	7476 (22)	−2574 (15)	3953 (13)	126	12827 (21)	−2489 (11)	10116 (11)	75
O*A*(3′)	8124 (15)	−2126 (9)	3745 (11)	145	13573 (13)	−1980 (8)	10029 (9)	101
C*M*(3′)	7819 (21)	−3358 (10)	4265 (11)	69	13143 (20)	−3263 (10)	10291 (12)	65
C(4′)	5069 (18)	−1840 (10)	3029 (9)	38	11015 (20)	−1649 (10)	8793 (9)	50
O(4′)	5707 (11)	−2001 (7)	2336 (6)	59	12053 (13)	−1543 (6)	8362 (6)	75
C*A*(4′)	5500 (22)	−2625 (10)	1931 (11)	110	12616 (20)	−2117 (10)	8082 (11)	68
O*A*(4′)	4805 (18)	−3059 (9)	2165 (8)	125	12255 (13)	−2735 (7)	8137 (8)	92
C*M*(4′)	6154 (20)	−2694 (11)	1185 (9)	73	13691 (20)	−1925 (13)	7568 (13)	118
C(5′)	4365 (16)	−1129 (8)	2862 (8)	41	10224 (18)	−983 (10)	8570 (8)	52
O(5′)	3814 (12)	−928 (6)	3556 (6)	47	9216 (12)	−1010 (6)	9048 (6)	62
C(6′)	3553 (20)	−1213 (10)	2157 (12)	74	9911 (24)	−1051 (10)	7703 (12)	59
Cl(1)	5943 (9)	5051 (4)	469 (6)	200	10917 (14)	−249 (6)	5599 (5)	256
Cl(2)	3974 (10)	4553 (5)	1304 (4)	187	9011 (14)	−771 (8)	4897 (11)	328
Cl(3)	4036 (9)	4373 (5)	−334 (4)	150	11008 (13)	−634 (9)	4055 (6)	297
C(Cl)	4848 (25)	4400 (13)	476 (12)	106	10083 (28)	−145 (12)	4633 (13)	124
H(CCl)	539 (18)	397 (9)	50 (8)	123	1115 (20)	91 (11)	399 (9)	144
H(1)	380 (12)	47 (7)	374 (6)	44	857 (12)	30 (6)	966 (6)	31
H(2)	504 (14)	164 (7)	362 (7)	59	977 (12)	139 (6)	980 (6)	31
H(3)	728 (13)	79 (6)	415 (6)	52	1124 (13)	108 (7)	1097 (6)	51
H(4)	597 (13)	175 (7)	510 (6)	50	955 (12)	157 (6)	1118 (6)	37
H(5)	519 (12)	−1 (6)	538 (6)	46	996 (12)	−2 (6)	1140 (6)	39
H(61)	583 (14)	94 (8)	694 (7)	68	911 (15)	34 (8)	1274 (7)	73
H(62)	487 (14)	93 (7)	642 (7)	68	815 (15)	34 (8)	1205 (7)	73
H(1′)	389 (12)	−71 (6)	472 (6)	34	883 (12)	−90 (6)	990 (6)	32
H(2′)	444 (12)	−194 (6)	484 (6)	43	960 (13)	−216 (7)	1018 (7)	52
H(3′)	643 (12)	−138 (7)	365 (6)	51	1172 (12)	−139 (6)	977 (6)	36
H(4′)	463 (12)	−211 (6)	328 (6)	36	1031 (13)	−212 (7)	864 (7)	51
H(5′)	479 (12)	−67 (6)	281 (6)	34	1060 (12)	−27 (7)	869 (6)	46
H(61′)	277 (14)	−166 (8)	238 (7)	76	1051 (14)	−107 (8)	700 (7)	74
H(62′)	397 (14)	−148 (7)	169 (7)	76	960 (14)	−129 (8)	760 (7)	74

Bond distances and angles

The standard deviations of the bond distances are 0·02 Å for C–Br, C–O and C–C ring distances and 0·03 Å for the acetate groups and C–Cl distances. The e.s.d.'s of the angles are 1° except for the acetate-group angles for which the e.s.d.'s are 2°. The bond distances and angles of the four molecules in the asymmetric units are normal and are given on Fig. 2. The extreme values of the equivalent bond distances and angles in the four chemically equivalent units are some 6σ different from each other. This is partly due to the fact that the number of observed reflections is very low compared to the number of refined parameters. The average C–Br distance of 1·977 Å (range 1·95–2·01 Å) agrees reasonably well with the average of 1·971 Å calculated using 34 values listed by Kennard *et al.* (1972). The endocyclic torsion angles, listed in Table 3, range from 49 (3) to 66 (3)°, values which are within the range tabulated by Arnott & Scott (1972).

The two glycosyl units in each 6,6'-dibromotrehalose hexaacetate molecule have been compared by means of the best-molecular-fit program of Nyburg (1969). Only when the ring atoms and those directly bonded to the ring are compared is there a reasonably good match. However, when the acetate-group atoms are included, important discrepancies appear. The fit, expressed by $(\sum \Delta^2)^{1/2}/n$, which is the average distance separating corresponding atoms when two equivalent parts of the molecules are best superposed, varies from 0·08 Å, for the six ring atoms plus the four atoms nearest to the ring, to 0·25 Å when all 20 equivalent atoms are matched.

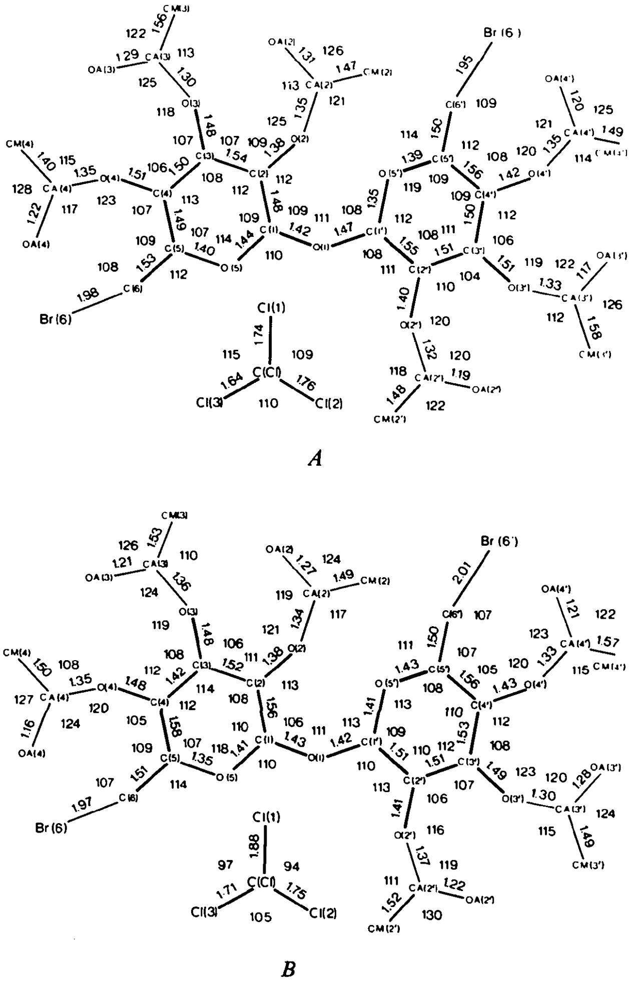


Fig. 2. Numbering of the atoms, bond distances and angles in the 6,6'-bromotrehalose hexaacetate and chloroform molecules.

Glycosidic linkage

The average glycosidic C(1)–O(1) distance of 1·435 (18) Å is not significantly different from that observed in both trehalose dihydrate [1·415 (3)–1·422 (3) Å] and in trehalose calcium bromide monohydrate [1·406 (6) Å]. The glycosidic bond angle, τ = C(1)–O(1)–C(1'), observed here is only 111·3 (12)° while the same angle is 115·8 (2) and 113·2 (3)° in the above trehalose derivatives respectively. Although the bridge angle has been observed with values ranging from 111 to 122°, in only three other compounds, all with the (1 → 6) linkage, were values close to 111° observed. This was in α-melibiose monohydrate, τ = 111·5 (2)° (Kanters, Roelofsen, Doesburg & Koops, 1976), planteose dihydrate, τ = 111·2 (2)° (Rohrer, 1972), and in raffinose pentahydrate, τ = 111·4 (5)° (Berman, 1970).

Table 3. *Torsion angles* (°)

Estimated standard deviations are about 3°. *A* (*B*), *A'* (*B'*) refer to the unprimed and primed rings of molecule *A* (*B*).

	A	*A'*	*B*	*B'*
Torsion angles about the glycosidic bond				
C(1)–O(1)–C(1')–O(5')	79	74	77	80
C(1)–O(1)–C(1')–C(2')	−159	−167	−160	−161
Endocyclic torsion angles				
O(5)–C(1)–C(2)–C(3)	54	52	49	58
C(1)–C(2)–C(3)–C(4)	−52	−55	−50	−52
C(2)–C(3)–C(4)–C(5)	54	57	53	50
C(3)–C(4)–C(5)–O(5)	−59	−54	−54	−53
C(4)–C(5)–O(5)–C(1)	62	57	60	63
C(5)–O(5)–C(1)–C(2)	−61	−57	−61	−66
Exocyclic torsion angles				
O(1)–C(1)–C(2)–C(3)	−65	−67	−69	−67
O(1)–C(1)–O(5)–C(5)	57	62	55	57
O(2)–C(2)–C(3)–C(4)	−176	−176	−174	−174
O(2)–C(2)–C(1)–O(5)	177	173	172	176
O(3)–C(3)–C(4)–C(5)	169	170	170	166
O(3)–C(3)–C(2)–C(1)	−166	−168	−168	−169
O(4)–C(4)–C(5)–O(5)	−175	−175	−176	−174
O(4)–C(4)–C(3)–C(2)	172	176	171	166
O(4)–C(4)–C(5)–C(6)	63	59	60	66
C(6)–C(5)–O(5)–C(1)	−178	−179	−178	−179
C(6)–C(5)–C(4)–C(3)	180	180	−178	−174
Br(6)–C(6)–C(5)–C(4)	177	−177	−176	178
Br(6)–C(6)–C(5)–O(5)	58	60	65	59

The torsion angles describing the glycosidic linkage, C(1)–O(1)–C(1′)–O(5′) and C(1)–O(1)–C(1′)–C(2′), average 78 (3) and −162 (3)° respectively. These two values are in excellent agreement with those found by Cook & Bugg (1973) in trehalose calcium bromide monohydrate [77·0 (5), −164·6 (5)°]* but differ very significantly from the values of 61·7 (2) and −177·0 (2)° observed by Brown *et al.* (1972) in trehalose dihydrate.

Acetate groups

The fact that when the acetate groups are taken into account the two pyranose rings of each molecule do not superpose well is clearly demonstrated in Table 4, where the orientations of the acetate groups are compared through the torsion angles C($X-1$)–C(X)–O(X)–CA(X) and C($X+1$)–C(X)–O(X)–CA(X). The orientations of the acetate groups all fall within a 55° range. Although these differences in the orientations of the acetate groups are large, they are not uncommon in acetylated glycosyl derivatives. For example in *β*-D-acetylcellobiose these torsion angles range from 85 to 145° (Leung, Chanzy, Pérez & Marchessault, 1976) and from 95 to 145° in tri-*O*-acetyl-*α*-D-xylopyranosylazide (Lugar & Paulsen, 1974).

Chloroform molecules

The C–Cl distances, ranging from 1·635 (24) to 1·877 (27) Å (average 1·746 Å), and the Cl–C–Cl angles with an average of 105° are reasonably close to the values of 1·762 Å and 110·9° which were found for chloroform by microwave spectroscopy (Wolfe, 1956).

All the atoms of both chloroform molecules have thermal parameters three to four times larger than those of the other atoms. This and the fact that the extreme values of the bond distances and angles are 6 and 10σ apart respectively is indicative of the high thermal motion of the chloroform molecules. This observation is consistent with the fact that the crystals decompose very easily in air by loss of solvent.

Table 4. *Orientations of the acetate groups* (°)

A (*B*), *A*′ (*B*′) refer to the unprimed and primed rings of molecule *A* (*B*) in Fig. 2.

	A	*A*′	*B*	*B*′
C(1)–C(2)–O(2)–*CA*(2)	94	123	84	95
C(3)–C(2)–O(2)–*CA*(2)	−142	−118	−155	−145
C(2)–C(3)–O(3)–*CA*(3)	−139	−122	−112	−131
C(4)–C(3)–O(3)–*CA*(3)	106	121	125	109
C(3)–C(4)–O(4)–*CA*(4)	114	123	101	96
C(5)–C(4)–O(4)–*CA*(4)	−125	−118	−138	−145

Packing of the molecules

The existence of two molecules in the asymmetric unit shows that the trehalose moiety is fairly rigid and that it is only through the various orientations of the acetate substituents that the two molecules may be differentiated. There are no exceptionally short intermolecular contacts. Most of the closer contacts (3·10–3·30 Å) occur between atoms of the C(2) acetates.

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* The published values are in error; these have been recomputed from the atomic coordinates.

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