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Two Polymorphs of Structures of α,α -Trehalose Octaacetate Monohydrate

Young Ja Park* and Jung Mi Shin

Department of Chemistry, Sook Myung Women's University, Seoul 140-742

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Structures of two polymorphs of α,α -trehalose octaacetate monohydrate, $C_{28}H_{38}O_{19} \cdot H_2O$, have been studied by X-ray diffraction method. α,α -trehalose (α -D-glucopyranosyl α -D-glucopyranoside) is a nonreducing disaccharide. The polymorph I belongs to the monoclinic $P2_1$, and has unit cell parameters of $a=10.725(1)$, $b=15.110(4)$, $c=11.199(5)$ Å, $\beta=108.16(2)^\circ$ and $Z=2$. The polymorph II is orthorhombic $P2_12_12_1$, with $a=13.684(4)$, $b=15.802(4)$, $c=17.990(9)$ Å and $Z=4$. The final R and R_w values for monoclinic polymorph I are 0.043 and 0.048 and for orthorhombic polymorph II are 0.116 and 0.118, respectively. Those R values of polymorph II are high because the large thermal motions of acetyl groups and the poor quality of the crystal. The molecular conformations in the two polymorphs are similar. Both D-glucopyranosyl rings have chair 4C_1 conformations and atoms of glycosidic chain $\alpha(1\rightarrow1)$ linkage are coplanar. The primary acetate groups of the pyranose residues assume both gauche-*trans* conformations. The molecules of two polymorphs have pseudo- C_2 symmetry at glycosidic O(1) atom. The bond lengths and angles are normal compared with those in other acetylated sugar compounds. The molecules in the monoclinic crystal are held by the hydrogen bonds with the water molecules and by van der Waals forces.

Introduction

α,α -trehalose octaacetate, $C_{28}H_{38}O_{19}$ is a acetylated product of α,α -trehalose which is a nonreducing symmetrical disaccharides composed of two glucosyl residues bridged by an $\alpha(1\rightarrow1)$ linkage. α,α -trehalose derives its name from the trehala manna which forms the cocoons of a beetle of the *Laurinus* family. α,α -trehalose is relatively inert compared to many carbohydrates due to its nonreducing nature and stable glycosidic linkage, which is possibly why it has transport functions in some organisms¹.

X-ray crystal structure determinations of anhydrous α,α -trehalose², α,α -trehalose dihydrate^{3,4} and α,α -trehalose calcium bromide monohydrate⁵ have been already carried out.

The prime aim in this study is to examine the distortion of the ring arising from the introduction of the acetyl substituents, the variation of the conformation angles about the linkage oxygen and the molecular packing due to the suppression of the intra- and intermolecular hydrogen bonds which are present in the peracetylated crystal structure.

Experimental

2,3,4,6-tetra-O-acetyl-1-O-(2,3,4,6-tetra-O-acetyl- α -D-gluco-

pyranosyl)- α -D-glucopyranose(α,α -trehalose octaacetate) from Sigma Chemical Company crystallized as two polymorphs; the stable monoclinic and unstable orthorhombic form. The monoclinic crystals were obtained by slow evaporation from a mixture of an aqueous ethyl ether and cyclohexane (polymorph I). The orthorhombic crystals were grown by evaporation of an aqueous methanolic solution. But this crystal decomposes very easily in the air. Therefore the orthorhombic crystal was mounted on a thin-walled lead-free capillary (polymorph II).

X-ray measurements of the two polymorphs were performed on an Nonius CAD-4 diffractometer. The most relevant data collection parameters are reported in Table 1. The intensity data of the orthorhombic form showed crystal damage during the data collection, and therefore were corrected as indicated by 14% intensity decrease of the standard reflection. Intensities were corrected for Lorentz and polarization factors, but absorption was ignored.

The structures of two polymorphs were solved by direct methods of the program Shelxs-86⁶, and refined by Fourier and least-squares methods using Shelx-76⁶ program.

The parameters of the monoclinic polymorph I refined were the positional parameters of all atoms, anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal

Table 1. Summary of Crystal Data, Intensity Collection and Least-Squares Refinement Statistics for α,α -Trehalose Octaacetate Monohydrate

	Monoclinic polymorph I	Orthorhombic polymorph II
molecular formula	C ₂₈ H ₃₈ O ₁₉ ·H ₂ O	C ₂₈ H ₃₈ O ₁₉ ·H ₂ O
molecular weight	696.6	696.6
space group	P2 ₁	P2 ₁ 2 ₁ 2 ₁
a, Å	10.725(5)	13.684(4)
b, Å	15.110(4)	15.802(4)
c, Å	11.199(5)	17.999(9)
β , deg.	108.16(2)	
Z	2	4
V, Å ³	1724.5	3890.1
μ (Mo-K α), cm ⁻¹	0.75	0.67
density, g/cm ³	1.342 (calc.)	1.190 (calc.)
	1.33 (meas. by floatation in KI solution.)	
radiation	Mo-K α	Mo-K α
	(graphite monochromator, $\lambda=0.7107$ Å)	
crystal size, mm	0.2×0.8×0.7	0.3×0.5×0.5
cell constant	19 reflections	20 reflections
determination	(20<2 θ <34°)	(15<2 θ <22°)
2 θ range, deg.	2-50	2-52
scan type	ω -2 θ	ω -2 θ
scan range, deg.	0.6+0.35 tan θ	0.7+0.34 tan θ
no. of unique reflections	3066	3395
no. of observed reflections	2982, $ F_o >3\sigma F_c $	2284, $ F_o >3\sigma F_c $
R	0.043	0.116
R _w	0.048	0.118
weighting scheme	1/ $\sigma^2(F_o)+0.004(F_o)^2$, 2.3/ $\sigma^2(F_o)+0.005(F_o)^2$	

parameters for hydrogen atoms. The final difference Fourier synthesis showed maximum and minimum electron densities of 0.26 and -0.22 eÅ⁻³, respectively. The final R and R_w values were 0.043 and 0.048, respectively, for the 2982 observed reflections with $|F_o|>3\sigma|F_c|$.

For the orthorhombic polymorph II, in the first resulting E-map, and the atoms of the C(6') acetate group and water molecule were not found. The complete molecule was obtained after successive Fourier and difference Fourier syntheses. Three cycles of isotropic and four cycles of anisotropic full matrix least squares refinements reduced R to 0.14. At this stage, the highest peak in the difference map was located as water oxygen atom. The positions of all hydrogen atoms except those at the pyranosyl rings were calculated geometrically and fixed the temperature factors U_{iso} of 0.05 Å². The final R and R_w values are 0.116 and 0.118 for 2284 observed reflections. This high R value is attributed to the large thermal motions of acetyl groups as well as the poor quality of the crystal. The electron density map showed some residual density, the extreme fluctuations being 0.61 and -0.40 eÅ⁻³.

Table 2. Final Fractional Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å²×10³) of the Nonhydrogen Atoms for Monoclinic Polymorph I. The e.s.d.'s are in the Parentheses

$U_{eq} = 1/3\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$				
Atom	x	y	z	U _{eq}
C(1)	5764(3)	8809(2)	7088(3)	41(4)
C(2)	6816(3)	8091(2)	7432(3)	42(2)
C(3)	7124(3)	7812(2)	8794(3)	41(5)
C(4)	7445(3)	8629(2)	9626(3)	41(0)
C(5)	6411(3)	9351(2)	9204(3)	43(3)
C(6)	6904(4)	10204(2)	9912(3)	51(10)
O(1)	4594(2)	8439(0)	7188(2)	39(5)
O(2)	6378(2)	7314(2)	6666(2)	51(6)
O(3)	8252(2)	7246(2)	9092(2)	47(5)
O(4)	7498(2)	8381(2)	10884(2)	47(5)
O(5)	6177(2)	9547(1)	7897(2)	43(8)
O(6)	5892(2)	10860(2)	9589(2)	55(14)
C(A2)	6555(4)	7303(3)	5537(3)	62(9)
C(A3)	8255(3)	6501(2)	9758(3)	51(5)
C(A4)	8589(3)	8572(3)	11837(3)	53(8)
C(A6)	6054(4)	11558(2)	8902(4)	58(15)
O(A2)	7008(5)	7912(4)	5147(3)	102(28)
O(A3)	7342(3)	6274(2)	10077(3)	71(14)
O(A4)	9531(3)	8899(3)	11687(3)	87(37)
O(A6)	6965(3)	11623(2)	8510(4)	84(31)
C(M2)	6076(6)	6463(4)	4859(5)	82(16)
C(M3)	9538(4)	6029(3)	10051(5)	71(9)
C(M4)	8393(5)	8349(4)	13063(5)	69(21)
C(M6)	4988(5)	12217(4)	8723(6)	83(33)
C(1')	3453(3)	8955(2)	6608(2)	40(6)
C(2')	2294(3)	8478(2)	6813(2)	41(2)
C(3')	2206(3)	7550(2)	6273(3)	42(5)
C(4')	2149(3)	7606(2)	4882(3)	39(6)
C(5')	3178(3)	8224(2)	4657(2)	40(5)
C(6')	2840(3)	8436(2)	3276(3)	50(4)
O(2')	2463(2)	8420(2)	8135(2)	47(4)
O(3')	1001(2)	7156(2)	6308(2)	48(10)
O(4')	2437(2)	6733(1)	4509(2)	47(9)
O(5')	3230(2)	9049(1)	5306(2)	42(11)
O(6')	3923(2)	8895(2)	3056(2)	57(1)
C(A2')	1423(3)	8640(2)	8515(3)	52(5)
C(A3')	1008(3)	6307(3)	6690(3)	59(2)
C(A4')	1456(3)	6231(3)	3813(4)	59(10)
C(A6')	3742(4)	9743(3)	2662(3)	58(1)
O(A2')	393(3)	8851(3)	7826(3)	78(16)
O(A3')	1977(3)	5856(2)	7006(4)	94(36)
O(A4')	349(3)	6482(3)	3438(4)	109(41)
O(A6')	2735(3)	10127(2)	2485(3)	77(23)
C(M2')	1770(5)	8582(5)	9912(4)	87(26)
C(M3')	-324(5)	5998(4)	6567(6)	87(23)
C(M4')	1907(5)	5329(3)	3622(6)	83(28)
C(M6')	4934(6)	10121(5)	2466(7)	98(20)
O(W)	-2228(4)	5705(3)	2629(4)	102(5)

Table 3. Final Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) of the Nonhydrogen Atoms for Orthorhombic Polymorph II. The e.s.d.'s are in the Parentheses

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
C(1)	2820(10)	4537(7)	2465(5)	56(28)
C(2)	2450(9)	5010(7)	3160(6)	53(15)
C(3)	2939(8)	5862(7)	3233(5)	47(18)
C(4)	4028(9)	5769(7)	3222(6)	61(22)
C(5)	4344(8)	5232(8)	2527(7)	59(15)
C(6)	5369(12)	5033(9)	2580(10)	104(15)
O(1)	2509(5)	5006(4)	1849(3)	48(13)
O(2)	1412(5)	5172(5)	3118(4)	61(7)
O(3)	2641(6)	6201(4)	3930(4)	59(23)
O(4)	4476(6)	6561(5)	3132(4)	64(7)
O(5)	3821(5)	4455(4)	2507(4)	51(1)
O(6)	5691(10)	4641(7)	1903(8)	127(11)
C(A2)	806(11)	4591(11)	3406(7)	77(17)
C(A3)	2297(11)	7003(9)	3961(7)	74(30)
C(A4)	4863(10)	6939(8)	3710(9)	76(22)
C(A6)	6522(17)	4912(21)	1575(12)	154(31)
O(A2)	1138(7)	3932(7)	3655(6)	93(10)
O(A3)	2303(13)	7463(6)	3458(6)	130(96)
O(A4)	4855(9)	6600(7)	4337(6)	112(36)
O(A6)	6911(17)	5548(13)	1726(13)	221(35)
C(M2)	-199(10)	4760(12)	3418(9)	106(35)
C(M3)	1996(11)	7231(8)	4747(8)	80(20)
C(M4)	5339(13)	7717(11)	3549(10)	113(7)
C(M6)	6762(17)	4381(17)	893(12)	154(34)
C(1')	2482(10)	4493(7)	1193(5)	61(22)
C(2')	2482(11)	5114(6)	532(6)	58(30)
C(3')	1531(8)	5590(7)	495(5)	49(12)
C(4')	679(9)	5056(7)	548(6)	57(23)
C(5')	753(10)	4428(8)	1217(6)	68(27)
C(6')	-41(10)	3782(8)	1199(7)	80(16)
O(2')	3253(6)	5712(5)	568(4)	64(7)
O(3')	1541(6)	6000(5)	-234(4)	64(16)
O(4')	-168(6)	5570(6)	714(4)	77(18)
O(5')	1672(6)	3979(4)	1155(4)	55(7)
O(6')	-64(8)	3378(6)	1926(5)	99(28)
C(A2')	4130(14)	5483(10)	340(8)	83(31)
C(A3')	1490(9)	6854(7)	-273(7)	62(18)
C(A4')	-759(14)	5758(11)	156(10)	107(19)
C(A6')	12(16)	2519(12)	1966(10)	114(34)
O(A2')	4307(7)	4789(8)	157(7)	107(23)
O(A3')	1345(10)	7274(5)	251(5)	112(68)
O(A4')	-664(11)	5534(9)	-448(7)	147(34)
O(A6')	152(13)	2125(8)	1425(9)	151(53)
C(M2')	4885(11)	6132(11)	390(8)	99(19)
C(M3')	1496(12)	7118(7)	-1067(7)	83(38)
C(M4')	-1555(13)	6382(11)	426(11)	120(15)
C(M6')	-101(16)	2173(11)	2692(10)	123(21)
O(W)	6878(22)	2946(16)	3248(13)	285(39)

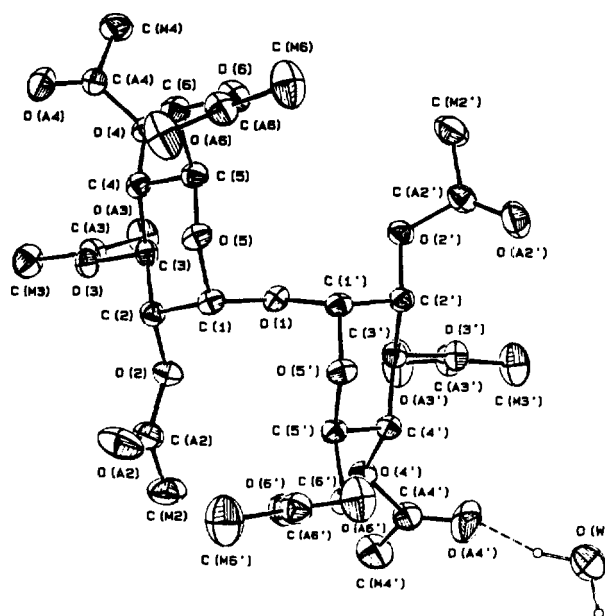


Figure 1. Conformation and atomic numbering of α,α -trehalose octaacetate monohydrate (monoclinic polymorph). The dashed line is the hydrogen bond.

The final positional parameters of the nonhydrogen atoms of two polymorphs are listed in Tables 2 and 3*.

Description of the Structures. The overall molecular conformation of two polymorphs is very similar. Therefore, we discuss mainly for the stable monoclinic polymorph I.

The molecular conformation of trehalose octaacetate monohydrate (polymorph I) and the numbering of the atoms are shown in Figure 1. The atoms in the acetate groups have been labeled CA, OA, and CM. These abbreviations stand for the carbonyl C, the carbonyl O, and the methyl C, respectively.

The bond distances and angles of the two polymorphs are given in Tables 4 and 5. The C-C bond lengths of the two pyranose residues are in the range of 1.509-1.541 Å. As in many pyranosides⁷, the exocyclic C(5')-C(6') bond length (1.509 Å) is significantly ($\geq 7\sigma$) shorter than the other C-C bond lengths. The C-O bond distances range from 1.410 to 1.446 Å. The C-O bond distances associated with the anomeric carbon atoms and the ring oxygen atoms show systematic trends similar to those observed in other α -pyranose sugar⁸. The axial C(1)-O(1) and C(1')-O(1) are 1.410(4) and 1.426(3) Å, respectively, and the two C-O bond lengths inside the unprimed ring, C(5)-O(5) (1.437(4) Å) and C(1)-O(5) (1.417(4) Å), are apparently different by 5σ . This feature is also the same in the primed pyranose ring. The C(5')-O(5') (1.436(3) Å) is lengthened and the C(1')-O(5') (1.410(3) Å) is shortened ($\geq 8\sigma$) in the C-O bonds involved in the C-O-C-O-C-O-C system.

The bond angles inside the rings range from 108.8(2) to 113.8(2) $^\circ$ and those outside the rings range from 106.1(2) to 111.7(2) $^\circ$. The angles at the ring oxygen atom, C(5)-O(5)-

*Tables for the anisotropic thermal parameters of the non-hydrogen atoms, coordinates of hydrogen atoms, and structure factor tables are available from the author (YJP).

Table 4. Bond Lengths (Å) of the Nonhydrogen Atoms for α,α -Trehalose Octaacetate Monohydrate. The e.s.d.'s are in the Parentheses

	Monoclinic polymorph I	Orthorhombic polymorph II
C(1)-C(2)	1.526(4)	1.54(2)
C(2)-C(3)	1.516(5)	1.51(2)
C(3)-C(4)	1.519(4)	1.50(2)
C(4)-C(5)	1.523(4)	1.57(2)
C(5)-C(6)	1.520(4)	1.44(2)
C(1')-C(2')	1.514(4)	1.54(1)
C(2')-C(3')	1.519(4)	1.51(2)
C(3')-C(4')	1.541(5)	1.44(2)
C(4')-C(5')	1.526(4)	1.56(2)
C(5')-C(6')	1.509(4)	1.49(2)
C(1)-O(1)	1.410(4)	1.40(1)
C(2)-O(2)	1.445(4)	1.44(2)
C(3)-O(3)	1.434(4)	1.43(1)
C(4)-O(4)	1.442(4)	1.40(1)
C(1)-O(5)	1.417(4)	1.38(2)
C(5)-O(5)	1.437(4)	1.42(1)
C(6)-O(6)	1.431(4)	1.44(2)
C(1')-O(1')	1.426(3)	1.43(1)
C(2')-O(2')	1.437(3)	1.42(2)
C(3')-O(3')	1.434(4)	1.46(1)
C(4')-O(4')	1.446(3)	1.45(2)
C(1')-O(5')	1.410(3)	1.38(2)
C(5')-O(5')	1.436(3)	1.45(2)
C(6')-O(6')	1.439(4)	1.46(2)
O(2)-C(A2)	1.337(4)	1.34(2)
O(3)-C(A3)	1.350(4)	1.35(2)
O(4)-C(A4)	1.347(4)	1.31(2)
O(6)-C(A6)	1.348(4)	1.35(3)
O(2')-C(A2')	1.354(4)	1.32(2)
O(3')-C(A3')	1.351(5)	1.35(1)
O(4')-C(A4')	1.333(4)	1.32(2)
O(6')-C(A6')	1.350(5)	1.36(2)
C(A2)-O(A2)	1.185(7)	1.22(2)
C(A3)-O(A3)	1.193(4)	1.16(2)
C(A4)-O(A4)	1.183(5)	1.25(2)
C(A6)-O(A6)	1.194(5)	1.17(4)
C(A2')-O(A2')	1.177(4)	1.17(2)
C(A3')-O(A3')	1.200(5)	1.17(2)
C(A4')-O(A4')	1.191(5)	1.15(2)
C(A6')-O(A6')	1.187(5)	1.17(2)
C(A2)-C(M2)	1.486(7)	1.40(2)
C(A3)-C(M3)	1.492(5)	1.52(2)
C(A4)-C(M4)	1.492(5)	1.42(2)
C(A6)-C(M6)	1.483(7)	1.52(4)
C(A2')-C(M2')	1.493(5)	1.46(2)
C(A3')-C(M3')	1.468(6)	1.49(2)
C(A4')-C(M4')	1.484(6)	1.55(3)
C(A6')-C(M6')	1.477(8)	1.42(3)
mean value O-CA	1.346(7)	1.34(2)
CA-OA	1.189(7)	1.18(3)
CA-CM	1.484(8)	1.47(5)

Table 5. Bond Lengths (°) of the Nonhydrogen Atoms for α,α -Trehalose Octaacetate Monohydrate. The e.s.d.'s are in the Parentheses

	Monoclinic polymorph I	Orthorhombic polymorph II
(a) inside the pyranose rings		
C(1)-C(2)-C(3)	111.3(3)	111(1)
C(2)-C(3)-C(4)	109.1(2)	111(1)
C(3)-C(4)-C(5)	112.8(3)	110(1)
O(4)-C(5)-O(5)	110.0(2)	110(1)
C(5)-O(5)-C(1)	114.1(2)	115(1)
C(5)-C(1)-C(2)	109.8(2)	109(1)
C(1')-C(2')-C(3')	109.4(2)	111(1)
C(2')-C(3')-C(4')	109.3(2)	114(1)
C(3')-C(4')-C(5')	113.4(2)	112(1)
C(4')-C(5')-O(5')	111.3(2)	108(1)
C(5')-O(5')-C(1')	113.8(2)	114(1)
O(5')-C(1')-C(2')	108.8(2)	109(1)
(b) outside the pyranose rings		
O(5)-C(1)-O(1)	111.7(2)	113(1)
C(2)-C(1)-O(1)	107.2(2)	107(1)
C(1)-C(2)-O(2)	110.5(2)	112(1)
C(3)-C(2)-O(2)	107.4(2)	106(1)
C(2)-C(3)-O(3)	107.7(2)	107(1)
C(4)-C(3)-O(3)	109.1(3)	109(1)
C(3)-C(4)-O(4)	108.7(3)	110(1)
C(5)-C(4)-O(4)	107.0(2)	106(1)
C(4)-C(5)-C(6)	110.2(3)	109(1)
O(5)-C(5)-C(6)	106.1(2)	108(1)
C(5)-C(6)-O(6)	110.1(3)	110(1)
O(5')-C(1')-O(1')	111.7(2)	113(1)
C(2')-C(1')-O(1')	107.4(2)	106(1)
C(1')-C(2')-O(2')	109.8(2)	113(1)
C(3')-C(2')-O(2')	109.0(2)	108(1)
C(2')-C(3')-O(3')	108.5(3)	105(1)
C(4')-C(3')-O(3')	107.4(2)	109(1)
C(3')-C(4')-O(4')	107.3(2)	109(1)
C(5')-C(4')-O(4')	106.2(2)	104(1)
C(4')-C(5')-C(6')	110.2(2)	112(1)
O(5')-C(5')-C(6')	107.0(2)	107(1)
C(5')-C(6')-O(6')	109.2(2)	107(1)
(c) glycosidic bridge		
C(1)-O(1)-C(1')	114.0(2)	111(1)
(d) acetate groups		
C(2)-O(2)-C(A2)	117.1(3)	118(1)
C(3)-O(3)-C(A3)	118.9(2)	119(1)
C(4)-O(4)-C(A4)	118.5(2)	120(1)
C(6)-O(6)-C(A6)	117.6(3)	119(2)
C(2')-O(2')-C(A2')	117.2(2)	119(1)
C(3')-O(3')-C(A3')	119.1(2)	117(1)
C(4')-O(4')-C(A4')	119.1(3)	119(1)
C(6')-O(6')-C(A6')	118.1(3)	118(1)

O(2)-C(A2)-O(A2)	122.4(4)	120(1)
O(3)-C(A3)-O(A3)	123.0(3)	124(1)
O(4)-C(A4)-O(A4)	123.2(3)	121(1)
O(6)-C(A6)-O(A6)	122.7(3)	124(2)
O(2')-C(A2')-O(A2')	123.8(3)	122(2)
O(3')-C(A3')-O(A3')	123.4(3)	122(1)
O(4')-C(A4')-O(A4')	122.9(4)	125(2)
O(6')-C(A6')-O(A6')	123.3(4)	120(2)
O(2)-C(A2)-C(M2)	111.4(4)	119(1)
O(3)-C(A3)-C(M3)	111.3(3)	111(1)
O(4)-C(A4)-C(M4)	110.1(3)	115(1)
O(6)-C(A6)-C(M6)	111.8(4)	111(2)
O(2')-C(A2')-C(M2')	110.7(3)	116(1)
O(3')-C(A3')-C(M3')	111.3(3)	109(1)
O(4')-C(A4')-C(M4')	111.9(3)	110(1)
O(6')-C(A6')-C(M6')	111.9(4)	115(2)
O(A2)-C(A2)-C(M2)	126.2(4)	122(2)
O(A3)-C(A3)-C(M3)	125.7(3)	125(1)
O(A4)-C(A4)-C(M4)	126.7(3)	124(1)
O(A6)-C(A6)-C(M6)	125.5(4)	124(2)
O(A2')-C(A2')-C(M2')	125.5(4)	122(2)
O(A3')-C(A3')-C(M3')	125.1(4)	128(1)
O(A4')-C(A4')-C(M4')	125.1(4)	125(2)
O(A6')-C(A6')-C(M6')	124.8(5)	125(2)
mean value C-O-CA	118.2(8)	119(1)
O-CA-OA	123.1(4)	122(2)
O-CA-OM	111.3(6)	113(3)
OA-CA-CM	125.6(6)	124(2)

C(1) and C(5')-O(5')-C(1'), are 114.1(2) and 113.8(2)°, respectively. The angles at anomeric carbon atom, O(5)-C(1)-O(1) and O(5')-C(1')-O(1), are both 111.7(2)°.

An important stereochemical feature in molecular geometry is the value of the glycosidic bond angle. The C(1)-O(1)-C(1') glycosidic bridge angle of 114.0(2)° are comparable with those found in trehalose related compounds; 113.3(4)° in anhydrous trehalose, 115.7(3)° in trehalose dihydrate, 113.2(3)° in trehalose · CaBr₂ · H₂O.

The average bond distances and angles of the acetate groups are in good agreement with the normal values observed with other acetylated carbohydrate derivatives^{9,10}. The conformations of the C(2)-O(2) and C(6)-O(6) bonds are different in two polymorphs. The torsion angles, C(3)-C(2)-O(2)-C(A2) and C(5)-C(6)-O(6)-C(A6) are 153.7(4) and -110.6(4)° for the monoclinic form and -148(1) and 133(2)° for the orthorhombic form. The atoms of C, O, C(A), O(A) and C(M) are nearly coplanar and these planes are approximately perpendicular (79°-85°) to the mean plane of the pyranose rings.

The torsion angles are given in Table 6. Each D-glucopyranosyl ring has the ⁴C₁ chair conformation. The torsion angles in the unprimed pyranosyl ring range from 51.1 to 60.5°, whereas those of the primed ring have a wider range of 46.2°-64.6°. The torsion angles around the glycosidic bonds, O(5)-C(1)-O(1)-C(1') and C(1)-O(1)-C(1')-O(5'), are 73.8(3) and 61.5(2)°, C(2)-C(1)-O(1)-C(1') and C(1)-O(1)-C(1')

Table 6. Torsion Angles (°) for Trehalose Octaacetate Monohydrate. The e.s.d.'s are in the Parentheses

	Monoclinic polymorph I	Orthorhombic polymorph II
(a) inside the pyranose rings		
O(5)-C(1)-C(2)-C(3)	57.3(3)	57(1)
C(1)-C(2)-C(3)-C(4)	-52.7(3)	-54(1)
C(2)-C(3)-C(4)-C(5)	51.1(3)	52(1)
C(3)-C(4)-C(5)-O(5)	-52.8(3)	-53(1)
C(4)-C(5)-O(5)-C(1)	58.1(3)	60(1)
C(5)-O(5)-C(1)-C(2)	-60.5(3)	-61(1)
O(5')-C(1')-C(2')-C(3')	63.7(2)	54(1)
C(1')-C(2')-C(3')-C(4')	-54.9(3)	-49(1)
C(2')-C(3')-C(4')-C(5')	47.2(3)	49(1)
C(3')-C(4')-C(5')-O(5')	-46.2(2)	-53(1)
C(4')-C(5')-O(5')-C(1')	55.6(2)	62(1)*
C(5')-O(5')-C(1')-C(2')	-64.6(2)	-63(1)
(b) outside the pyranose rings		
O(1)-C(1)-C(2)-C(3)	-64.6(3)	-66(1)
O(1)-C(1)-C(2)-O(2)	54.7(2)	53(1)
O(5)-C(1)-C(2)-O(2)	176.6(3)	176(1)
C(1)-C(2)-C(3)-O(3)	-171.1(3)	-173(1)
O(2)-C(2)-C(3)-C(4)	-173.8(3)	-176(1)
O(2)-C(2)-C(3)-O(3)	67.8(3)	65(1)
C(2)-C(3)-C(4)-O(4)	169.5(3)	168(1)
O(3)-C(3)-C(4)-C(5)	168.5(3)	169(1)
O(3)-C(3)-C(4)-O(4)	-73.1(3)	-75(1)
C(3)-C(4)-C(5)-C(6)	-169.4(4)	-171(1)
O(4)-C(4)-C(5)-C(6)	71.1(3)	70(1)
O(4)-C(4)-C(5)-O(5)	-172.2(3)	-172(1)
C(1)-O(5)-C(5)-C(6)	177.2(3)	179(1)
C(5)-O(5)-C(1)-O(1)	59.0(2)	57(1)
O(1)-C(1')-C(2')-C(3')	-57.4(2)	-69(1)
O(1)-C(1')-C(2')-O(2')	62.2(2)	52(1)*
O(5')-C(1')-C(2')-O(2')	-176.7(3)	175(1)
C(1')-C(2')-C(3')-O(3')	-171.7(3)	-168(1)
O(2')-C(2')-C(3')-C(4')	-175.0(3)	-173(1)
O(2')-C(2')-C(3')-O(3')	68.2(3)	68(1)
C(2')-C(3')-C(4')-O(4')	164.2(3)	164(1)
O(3')-C(3')-C(4')-C(5')	164.7(3)	166(1)
O(3')-C(3')-C(4')-O(4')	-78.4(3)	-79(1)
C(3')-C(4')-C(5')-C(6')	-164.8(3)	-171(1)*
O(4')-C(4')-C(5')-C(6')	77.6(3)	71(1)*
O(4')-C(4')-C(5')-O(5')	-163.8(3)	-171(1)*
C(1')-O(5')-C(5')-C(6')	176.0(3)	-178(1)
C(5')-O(5')-C(1')-O(1)	53.8(2)	55(1)
(c) primary groups		
O(5)-C(5)-C(6)-O(6)	65.6(3)	68(1)
C(4)-C(5)-C(6)-O(6)	-175.4(4)	-172(2)
O(5')-C(5')-C(6')-O(6')	68.3(2)	76(1)*
C(4')-C(5')-C(6')-O(6')	-170.5(3)	-166(1)
(d) glycosidic bond		
O(5)-C(1)-O(1)-C(1')	73.8(3)	82(1)*

C(2)-C(1)-O(1)-C(1)'	-165.5(3)	-158(1)
O(5)-C(1)-O(1)-C(1)	61.5(2)	79(1)*
C(2)-C(1)-O(1)-C(1)	-179.2(3)	-161(1)*
(e) acetate groups		
C(1)-C(2)-O(2)-C(A2)	84.6(3)	91(1)*
C(3)-C(2)-O(2)-C(A2)	153.7(4)	-148(1)**
C(2)-C(3)-O(3)-C(A3)	-136.3(4)	-131(1)*
C(4)-C(3)-O(3)-C(A3)	105.3(3)	110(1)*
C(3)-C(4)-O(4)-C(A4)	125.4(4)	102(1)*
C(5)-C(4)-O(4)-C(A4)	-112.5(3)	-139(1)*
C(5)-C(6)-O(6)-C(A6)	-110.6(4)	133(2)**
C(1)-C(2)-O(2)-C(A2)'	133.1(3)	81(1)*
C(3)-C(2)-O(2)-C(A2)'	-107.1(3)	-156(2)*
C(2)-C(3)-O(3)-C(A3)'	-136.7(4)	-120(1)*
C(4)-C(3)-O(3)-C(A3)'	105.3(3)	118(1)*
C(3)-C(4)-O(4)-C(A4)'	103.2(3)	101(1)
C(5)-C(4)-O(4)-C(A4)'	-135.2(3)	-139(1)
C(5)-C(6)-O(6)-C(A6)'	-114.6(4)	-125(2)*
C(2)-O(2)-C(A2)-O(A2)	-2.6(4)	-4(1)
C(3)-O(3)-C(A3)-O(A3)	2.6(3)	-7(1)
C(4)-O(4)-C(A4)-O(A4)	-3.4(4)	1(1)
C(6)-O(6)-C(A6)-O(A6)	3.7(4)	-15(2)*
C(2)-O(2)-C(A2)-O(A2)'	2.0(3)	-5(1)
C(3)-O(3)-C(A3)-O(A3)'	0.1(3)	-7(1)
C(4)-O(4)-C(A4)-O(A4)'	3.1(4)	1(2)
C(6)-O(6)-C(A6)-O(A6)'	-0.2(4)	5(2)
C(2)-O(2)-C(A2)-C(M2)	179.3(5)	176(2)
C(3)-O(3)-C(A3)-C(M3)	-176.2(4)	179(2)
C(4)-O(4)-C(A4)-C(M4)	174.1(4)	177(2)
C(6)-O(6)-C(A6)-C(M6)	-175.5(5)	177(3)
C(2)-O(2)-C(A2)-C(M2)'	-177.6(4)	180(2)
C(3)-O(3)-C(A3)-C(M3)'	-175.4(5)	-179(1)
C(4)-O(4)-C(A4)-C(M4)'	-174.4(5)	-174(2)
C(6)-O(6)-C(A6)-C(M6)'	-179.5(5)	-175(2)

*The angle difference is greater than 5°. **The signs of the torsion angles of two polymorphs are opposite each other.

Table 7. Comparison of Molecular Geometry of the Trehalose Compounds

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i> *
(a) primary groups (°)					
O(5)-C(5)-C(6)-O(6)	65.6	68	-72.1	-75.6	61.1
C(4)-C(5)-C(6)-O(6)	-175.4	-172	46.8	47.0	-177.9
O(5)-C(5)-C(6)-O(6)'	68.3	76	71.0	69.8	61.1
C(4)-C(5)-C(6)-O(6)'	-170.5	-166	-171.3	-168.2	-177.9
(b) glycosidic angle (°)					
C(1)-O(1)-C(1)'	114.0	111	133.3	115.7	113.2
(c) glycosidic bond lengths (Å)					
C(1)-O(1)	1.410	1.40	1.416	1.417	1.406
C(1)-O(1)	1.426	1.43	1.420	1.421	1.406

(d) glycosidic torsion angles (°)

O(5)-C(1)-O(1)-C(1)'	73.8	82	60.8	75.0	-11.2
C(2)-C(1)-O(1)-C(1)'	-165.5	-158	-177.3	-165.6	108.6
O(5)-C(1)-O(1)-C(1)	61.5	79	60.1	61.7	-11.2
C(2)-C(1)-O(1)-C(1)	-179.2	-161	-178.2	-177.9	108.6
H(1)-C(1)-O(1)-C(1)'	-48	-47	-57	-36	-43
C(1)-O(1)-C(1)-H(1)'	-59	-49	-58	-61	-43

(e) C(1)→C(1)' pseudotorsion angles(°)

O(5)-C(1)⋯C(1)-O(5)'	119.7	137	107.9	120.7	135.6
O(5)-C(1)⋯C(1)-C(2)'	-114.0	-83	-123.1	-110.2	-87.1
C(2)-C(1)⋯C(1)-O(5)'	-103.6	-81	-122.3	-103.4	-87.1
C(2)-C(1)⋯C(1)-C(2)'	22.7	59	6.7	25.6	50.2

^a monoclinic α,α -trehalose octaacetate monohydrate. ^b orthorhombic α,α -trehalose octaacetate monohydrate. ^c anhydrous α,α -trehalose. ^d α,α -trehalose dihydrate. ^e trehalose·CaBr₂·H₂O (The molecule has own C₂ symmetry.)

C(2') are -165.5(3) and -179.2(3)°, respectively. Therefore, atoms C(2), C(1), O(1), C(1') and C(2') have a zigzag conformation, and are nearly coplanar within ± 0.10 Å. To specify the relative conformation of the two glucopyranosyl rings, it is better to consider pseudotorsion angles about the line between C(1) and C(1') rather than the torsion angles about the two bonds of the glycosidic linkage. The differences between the pseudotorsion angles, C(2)-C(1)⋯C(1)-O(5)' and O(5)-C(1)⋯C(1)-C(2)' show 10.4° that the departure of the molecule from the symmetry of point group C₂ is slightly larger than those of anhydrous trehalose [see Table 7]. It is also possible to describe the ring-to-ring orientation in relation to the α -D(1→1') linkage through the conformational angles ϕ and ψ , which are $\phi = \text{H}(1)-\text{C}(1)-\text{O}(1)-\text{C}(1)' = -48^\circ$ and $\psi = \text{C}(1)-\text{O}(1)-\text{C}(1)-\text{H}(1)' = -59^\circ$, respectively.

The orientations of the two pyranose rings for the trehalose related compounds are shown in Figure 2. As predicted, both pyranose rings have approximately the same orientations and the conformation of the primary group of the unprimed residue differs from those of anhydrous trehalose and trehalose dihydrate. They are both *gauche-trans*, whilst those in anhydrous trehalose and in trehalose dihydrate are *gauche-gauche* and *gauche-trans*, respectively. The two glucose residues are approximately related by a twofold symmetry through the O(1) atom.

The molecular packing in the peracetate carbohydrate crystals appeared to be determined mainly by the hydrogen bonds. In the acetate compounds, there is no intra- and intermolecular hydrogen bond because it is introduced by the acetyl substituents. But the carbonyl O(A) atoms serve as hydrogen bond acceptors. Thus, the water molecule O(W) of the trehalose octaacetate monohydrate (polymorph I) acts as a bridge between O(A3) (at $x-1, y, z-1$) and O(A4') and the sequence is O(A3)⋯H-O(W)-H⋯O(A4') [O(A3)⋯O(W): 2.880(5) Å; O(W)⋯O(A4'): 2.877(5) Å; O(A3)⋯H-O(W): 169(3)°; O(W)-H⋯O(A4'): 158(4)°].

The stereoscopic packing diagram for the monoclinic polymorph I is shown in Figure 3. The molecules are oriented with the pyranose rings approximately perpendicular to the *a* axis.

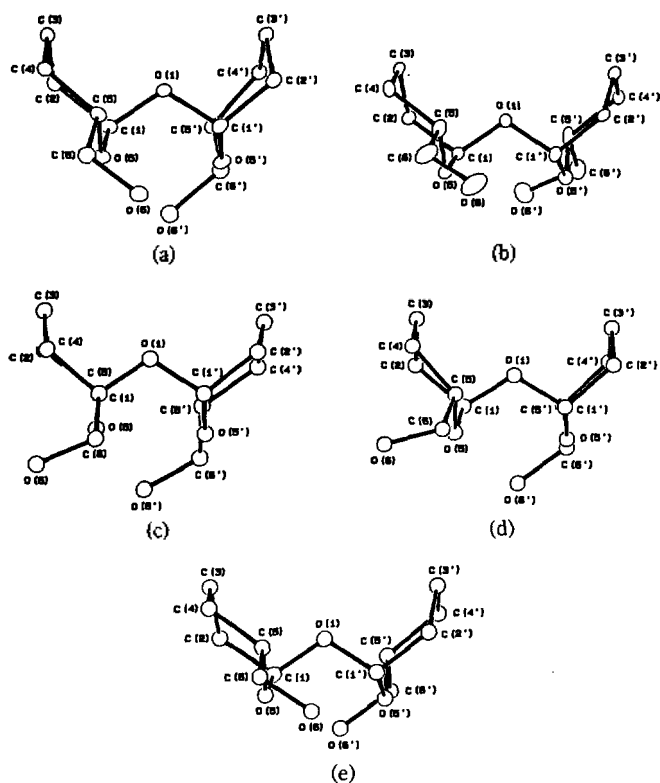


Figure 2. Ring orientations viewed perpendicular to the approximately twofold axis; (a) monoclinic α,α -trehalose octaacetate monohydrate (b) orthorhombic α,α -trehalose octaacetate monohydrate (c) anhydrous α,α -trehalose (d) α,α -trehalose dihydrate (e) trehalose \cdot CaBr₂ \cdot H₂O.

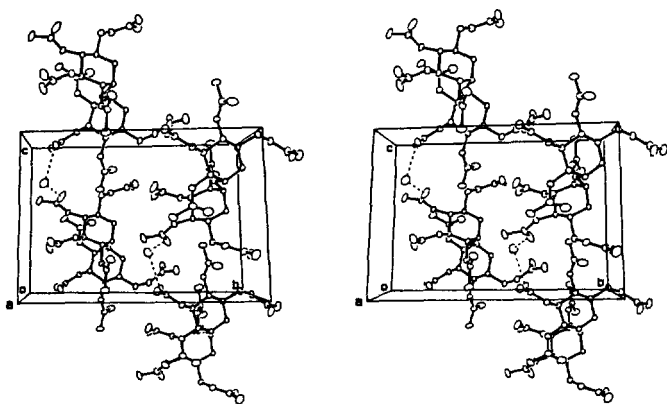


Figure 3. Stereoview of the monoclinic structure of α,α -trehalose octaacetate monohydrate. The dashed lines are the hydrogen bonds.

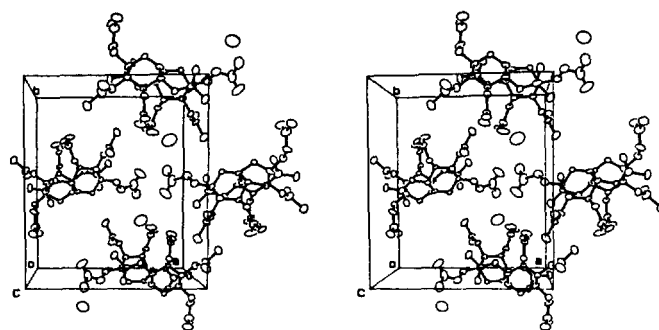


Figure 4. Stereoview of the orthorhombic structure of α,α -trehalose octaacetate monohydrate.

A stereoview of molecular packing for the orthorhombic polymorph II is shown in Figure 4. The orientations of the pyranose rings are approximately parallel to the ab plane. There is no particularly short intermolecular contacts except for $O(W) \cdots O(A3)$ (at $-x+1, y-0.5, -z+0.5$) distances (3.356 Å). The molecules are packed only by van der Waals forces.

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