The torsion angles $\theta$, $\varphi$ and $\psi$, frequently used to describe the conformations of glycosidic linkages as discussed above, are 174·8 (2), 177·4 (2) and −57·4 (2)°, respectively. The close agreement with the ideal values for a *trans–trans–gauche* conformation is obviously due to the restrictions of the molecular flexibility imposed by the attached dioxane ring.

The average endocyclic C—C bond length in the pyranose ring is 1·527 (12) Å, which agrees well with that, 1·526 (3) Å, calculated from the data on averaged glucopyranose rings. The average endocyclic bond angles are 110·4 (14)° for the pyranose ring and 109·8 (9)° for the dioxane ring. The largest angular deviation, 2·3°, from these averages occurs for C(3)–C(4)–C(5) and is possibly also the result of the molecular distortion caused by the interlayer hydrogen bonding.

After classifying carbohydrate molecules into two distinct types according to their $\theta$ and $\varphi$ values, *viz* the *gauche–gauche* ($52 \le \theta \le 67°$ and $75 \le \varphi \le 121°$) and *trans–gauche* ($171 \le \theta \le 193°$ and $-71 \le \varphi \le 105°$) types, Pérez & Marchessault (1978) have calculated the average geometries of the molecular fragment –C(5)–O(5)–C(1)–O(1)–. The present study concerns a molecule of a third class, the *trans–trans* type ($\theta = 174·8°$ and $\varphi = 177·4°$). Thus, the *exo*-anomeric effect, which stabilizes $\varphi$ values corresponding to a *gauche* conformation, has been eliminated in the present structure by formation of the dioxane ring. As shown in Table 6, the bond angles and bond distances are somewhat different from those of the other two types. Thus, the bond-angle distribution in 1,2-*O*-ethylene-β-D-glucopyranose resembles that of the *trans–gauche* type, while the bond-distance distribution is more similar to the *gauche–gauche* type.

### References


BERMAN, H. M., CHU, S. S. C. & JEFFREY, G. A. (1967). *Science*, **157**, 1576–1577.

BOLHUIS, F. VAN (1971). *J. Appl. Cryst.* **4**, 263–264.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

HELFERICH, B. & WERNER, J. (1942). *Chem. Ber.* **75**, 949.

*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99–102. Birmingham: Kynoch Press.

LEMIEUX, R. U., KOTO, S. & VOISIN, D. (1979). *Am. Chem. Soc. Symp. Ser.* No. 87, pp. 18–29.

PÉREZ, S. & MARCHESSAULT, R. H. (1978). *Carbohydr. Res.* **65**, 114–120.

SHELDRICK, B. & AKRIGG, D. (1980). *Acta Cryst.* B**36**, 1615–1621.

SHELDRICK, G. M. (1978). *SHELX* 78. A program for crystal structure determination. Univ. of Cambridge, England.

SUNDARALINGAM, M. (1968). *Biopolymers*, **6**, 189–213.

WOLFE, S., WHANGBO, M.-H. & MITCHELL, D. J. (1979). *Carbohydr. Res.* **69**, 1–26.


*Acta Cryst.* (1981). B**37**, 1693–1698

# Structure Determination of the Mannotrehalose Derivative 6-*O*-Acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranoside


BY PETER LUGER

*Institut für Kristallographie der Freien Universität Berlin, Takustrasse* 6, 1000 *Berlin* 33, *Federal Republic of Germany*

AND HANS PAULSEN

*Institut für Organische Chemie und Biochemie der Universität Hamburg, Martin-Luther-King-Platz* 6, 2000 *Hamburg* 13, *Federal Republic of Germany*


(*Received* 15 *October* 1980; *accepted* 27 *February* 1981)


### Abstract

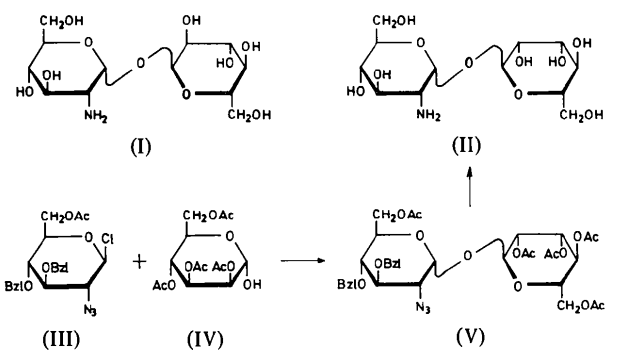
The crystal structure of the title compound, $C_{36}H_{43}N_3O_{15}$, $M_r = 757·8$, is orthorhombic, $P2_12_12_1$, with $a = 18·414$ (6), $b = 17·025$ (5), $c = 12·918$ (4) Å, $Z = 4$, $V_c = 4050$ (3) Å$^3$, $D_x = 1·235$ Mg m$^{-3}$, $\mu$(Cu $K\alpha$) = 0·833 mm$^{-1}$. The structure was solved by direct methods, and the data were refined to an $R$ value of 0·065 for 3802 reflections. In the C(5)–O(5)–C(1)–O(1)–C(1′)–O(5′)–C(5′) bond sequence, which is specific for carbohydrates of trehalose type, the C(1)–O bonds tend to be 0·2 Å shorter than the


0567-7408/81/091693-06$01.00

C(5)–O(5) bonds. The conformation around the glycosidic linkages is such that a twofold axis passes through O(1), *i.e.* C(1) is *trans* with respect to C(2′) of the opposite residue and *gauche* to the opposite ring O atom. All trehalose structures so far investigated have this conformational feature although their structures are otherwise different.

## Introduction

Trehalose is a sugar widely spread in nature. It is a non-reducing symmetrical disaccharide composed of two glucosyl residues bridged by an $\alpha,\alpha(1\rightarrow1)$ linkage. Trehalosamine (I), having one glycosyl residue replaced by glucosamine, was isolated from *Streptomyces virginiae* (Arcamone & Bizioli, 1957) and was found to have antibiotic properties. A mannotrehalosamine (II), having the second glucosyl residue replaced by mannose, was isolated later from a similar family of bacteria (Umezawa, 1974). The title compound (V) was an intermediate in the first synthesis of mannotrehalosamine (II), by the linkage of (III) and (IV) (Paulsen & Sumfleth, 1979).




In most of the oligosaccharides investigated so far by X-ray diffraction the glycosidic linkage is of type $1\rightarrow3$ or $1\rightarrow4$. There is little structural data known on the disaccharides of trehalose type, since single-crystal determinations have only been made of a dihydrate of $\alpha,\alpha$-trehalose itself (Brown, Rohrer, Berking, Beevers, Gould & Simpson, 1972; Taga, Senma & Osaki, 1972) and its calcium bromide (Cook & Bugg, 1973). The present work is the first structure analysis of a mannotrehalose derivative. The fully blocked derivative was studied in order to obtain information on the glycosidic $\alpha,\alpha(1\rightarrow1)$ linkage in a *gluco–manno* combination in the absence of hydrogen-bonding influences.

## Experimental

Large colourless tetrahedron crystals were obtained from a solution in ethanol/water. Preliminary lattice constants and the space group were determined from oscillation and Weissenberg photographs. Precise cell parameters (from 18 high-order axial reflections) and 3802 three-dimensional intensity data of an octant ($h,k,l$ all positive, $2\theta_{max} = 129°$) were measured on a DEC PDP 15 controlled Stoe diffractometer with Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å) using the $\omega$–$2\theta$ scan mode. The crystal used had an approximate size of 0·3 mm for each tetrahedron edge. The two reference reflections used for control and scaling of the intensities in the course of the data collection showed no significant variations. The most relevant crystallographic data are given in the *Abstract*.

The phase problem was solved by direct methods with the *MULTAN* program (Main, Woolfson & Germain, 1975). 350 reflections with $|E| > 1{\cdot}57$ and 6 reflections in the starting set were used to determine the structure. The trial having the largest combined figure of merit (2·93) yielded a structural model which showed 36 of the 54 non-hydrogen atoms at their correct positions. The missing atoms were determined from subsequent difference syntheses. The atomic parameters were refined by least-squares methods, using anisotropic temperature factors for the heavy atoms and isotropic temperature factors for the H atoms. In the first refinement stages the full-matrix mode was applied; with an increasing number of variables a subdivision of parameters into blocks of up to ten was necessary, each block being related to a chemically reasonable sub-fragment of the molecule. A weighting scheme which made $w\Delta F$ independent of $F_o$ and $\sin\theta$ was used. This was achieved by setting $w = xy$, with $x = 1$ for $\sin\theta > 0{\cdot}65$, $x = \sin\theta/0{\cdot}65$ otherwise and $y = 1$ for $F_o < 5{\cdot}0$, $y = 5{\cdot}0/F_o$ if $F_o \geq 5{\cdot}0$. Unobserved reflections (978 with $I < 2\sigma$) were included in the refinement only if $|F_c| > |F_o|$.

Scattering factors implemented in the corresponding routine of the XRAY 76 system (Stewart, Machin, Ammon, Dickinson, Heck & Flack, 1976) were used. After two cycles of anisotropic refinement the temperature factors of the acetoxy-group atoms at C(6) of the glucose fragment had diverged and become unusually large. A redetermination of that group from a difference synthesis yielded the same result. The temperature factors of the second anisotropic refinement cycle were then assigned to this acetoxy group and kept invariant in the following cycles. A similar behaviour of an acetoxy group at a C(6) carbohydrate carbon atom was observed in the refinement of β-D-acetylcellobiose (Leung, Chanzy, Pérez & Marchessault, 1976).

The H atoms at the pyranosyl rings were located with certainty from a difference synthesis; however, the methyl protons could only be identified after suitable maxima were compared with theoretically calculated H positions. In the *manno* part the 3- and 6-acetoxy groups appear to have disordered methyl groups with two orientations, one in a staggered position with respect to the carbonyl O and the other staggered to the

ester O atom, each orientation being approximately 50% occupied. This feature of the acetoxy groups has previously been observed several times (Kothe, Luger & Paulsen, 1976, 1979; Luger & Paulsen, 1974).

The final $R$ value ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) was 0·065 for the observed reflections and 0·084 for all reflections {$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0·090$}. The average shift/error ratio at the end of the refinement was 0·13. A final electron density map showed one peak of 0·5 e Å$^{-3}$ near the C(6) acetate group; all further residual density was below 0·3 e Å$^{-3}$.

The refinement and related calculations were executed on a CDC Cyber 175 computer (Wissenschaftliches Rechenzentrum Berlin) using the XRAY 76 system.

The fractional coordinates and an isotropic equivalent of the anisotropic temperature factors (Hamilton, 1959) of the non-hydrogen atoms are given in Table 1.*

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| C(1) | 1·0448 (4) | 0·3173 (3) | 0·2129 (5) | 6·9 (2) |
| C(2) | 0·9963 (4) | 0·3808 (3) | 0·1648 (5) | 6·9 (2) |
| C(3) | 0·9335 (4) | 0·3426 (4) | 0·1078 (5) | 7·5 (2) |
| C(4) | 0·9597 (4) | 0·2829 (3) | 0·0305 (5) | 6·9 (2) |
| C(5) | 1·0187 (4) | 0·2281 (3) | 0·0752 (4) | 6·6 (2) |
| O(5) | 1·0720 (2) | 0·2685 (2) | 0·1362 (3) | 7·0 (1) |
| N(21) | 0·9724 (4) | 0·4315 (3) | 0·2491 (5) | 9·7 (2) |
| N(22) | 0·9594 (4) | 0·4996 (3) | 0·2297 (5) | 8·8 (2) |
| N(23) | 0·9468 (6) | 0·5642 (4) | 0·2262 (6) | 12·1 (3) |
| O(30) | 0·8936 (3) | 0·4027 (3) | 0·0557 (4) | 8·8 (2) |
| C(31) | 0·8192 (4) | 0·4074 (7) | 0·0799 (9) | 10·6 (4) |
| C(32) | 0·7860 (4) | 0·4729 (5) | 0·0153 (6) | 9·1 (3) |
| C(33) | 0·8120 (6) | 0·5480 (6) | 0·0228 (10) | 12·3 (4) |
| C(34) | 0·7836 (9) | 0·6096 (9) | −0·0343 (14) | 15·2 (6) |
| C(35) | 0·7283 (12) | 0·5911 (14) | −0·1032 (14) | 16·3 (8) |
| C(36) | 0·7036 (10) | 0·5197 (20) | −0·1118 (14) | 20·0 (1) |
| C(37) | 0·7330 (6) | 0·4578 (10) | −0·0506 (11) | 14·0 (5) |
| O(40) | 0·9022 (3) | 0·2325 (3) | −0·0002 (4) | 8·5 (2) |
| C(41) | 0·8775 (7) | 0·2380 (6) | −0·1025 (7) | 10·4 (4) |
| C(42) | 0·8300 (5) | 0·1667 (5) | −0·1214 (6) | 9·4 (3) |
| C(43) | 0·7587 (7) | 0·1675 (10) | −0·0833 (12) | 13·4 (5) |
| C(44) | 0·7191 (10) | 0·1028 (2) | −0·0950 (19) | 19·0 (1) |
| C(45) | 0·7445 (15) | 0·0343 (14) | −0·1397 (18) | 21·0 (1) |
| C(46) | 0·8104 (12) | 0·0349 (7) | −0·1738 (12) | 18·5 (8) |
| C(47) | 0·8553 (8) | 0·1011 (7) | −0·1659 (8) | 12·2 (5) |
| C(6) | 1·0578 (5) | 0·1818 (4) | −0·0045 (6) | 8·5 (2) |
| O(60) | 1·0969 (3) | 0·2364 (3) | −0·0689 (4) | 10·0 (–) |
| C(61) | 1·1190 (7) | 0·2164 (7) | −0·1584 (8) | 12·3 (–) |
| O(61) | 1·0881 (7) | 0·1566 (7) | −0·1968 (7) | 12·3 (–) |
| C(62) | 1·1534 (8) | 0·2768 (8) | −0·2192 (9) | 14·3 (–) |
| O(1) | 0·9989 (2) | 0·2769 (2) | 0·2837 (3) | 6·2 (1) |
| C(1′) | 1·0341 (4) | 0·2397 (3) | 0·3665 (4) | 6·4 (2) |
| C(2′) | 0·9738 (3) | 0·1956 (3) | 0·4228 (5) | 6·4 (2) |
| C(3′) | 0·9247 (3) | 0·2541 (3) | 0·4777 (4) | 5·9 (2) |
| C(4′) | 0·9678 (3) | 0·3103 (3) | 0·5436 (5) | 6·1 (2) |
| C(5′) | 1·0234 (3) | 0·3508 (3) | 0·4768 (5) | 6·4 (2) |
| O(5′) | 1·0707 (2) | 0·2932 (2) | 0·4312 (3) | 6·7 (1) |
| O(20′) | 1·0076 (2) | 0·1471 (2) | 0·4993 (3) | 6·8 (1) |
| C(21′) | 0·9786 (4) | 0·0746 (3) | 0·5154 (5) | 7·7 (2) |
| O(21′) | 0·9322 (4) | 0·0478 (3) | 0·4618 (5) | 10·1 (2) |
| C(22′) | 1·0134 (6) | 0·0354 (5) | 0·6034 (7) | 10·8 (3) |
| O(30′) | 0·8737 (2) | 0·2136 (2) | 0·5439 (3) | 7·0 (1) |
| C(31′) | 0·8114 (4) | 0·1887 (5) | 0·5006 (7) | 8·8 (3) |
| O(31′) | 0·7979 (3) | 0·1966 (4) | 0·4120 (5) | 10·9 (2) |
| C(32′) | 0·7647 (5) | 0·1499 (8) | 0·5775 (9) | 13·3 (4) |
| O(40′) | 0·9165 (2) | 0·3675 (2) | 0·5817 (3) | 7·2 (1) |
| C(41′) | 0·9213 (4) | 0·3905 (4) | 0·6808 (5) | 8·0 (2) |
| O(41′) | 0·9690 (3) | 0·3696 (4) | 0·7371 (4) | 9·9 (2) |
| C(42′) | 0·8614 (5) | 0·4459 (6) | 0·7063 (9) | 12·3 (4) |
| C(6′) | 1·0727 (5) | 0·4067 (4) | 0·5351 (5) | 7·6 (2) |
| O(60′) | 1·1167 (2) | 0·4510 (2) | 0·4651 (4) | 7·7 (1) |
| C(61′) | 1·0866 (4) | 0·5164 (4) | 0·4254 (6) | 7·9 (2) |
| O(61′) | 1·0262 (3) | 0·5360 (3) | 0·4448 (5) | 9·7 (2) |
| C(62′) | 1·1380 (5) | 0·5580 (5) | 0·3557 (8) | 10·7 (3) |

## Discussion

A model of the molecular structure is shown in Fig. 1, which also gives the atom-numbering scheme (atoms belonging to the *gluco* and *manno* parts of the molecule are denoted by unprimed and single-primed numbers, respectively). Both pyranosyl rings are in the $^4C_1$ (D) conformation. As indicated by the torsion angles (Table 2) and the Cremer & Pople (1975) puckering parameters (the numerical values are $Q = 0·522$ Å, $\theta = 11·56°$ and $\varphi = 90·36°$ for *gluco* and $Q = 0·563$ Å, $\theta = 5·43°$, $\varphi = 276·11°$ for *manno*; Jeffrey & Yates, 1979), both rings are slightly distorted, the *manno* ring towards a $^4H_5$ conformation and the *gluco* ring in the

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters, and detailed tables of bond distances and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36087 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

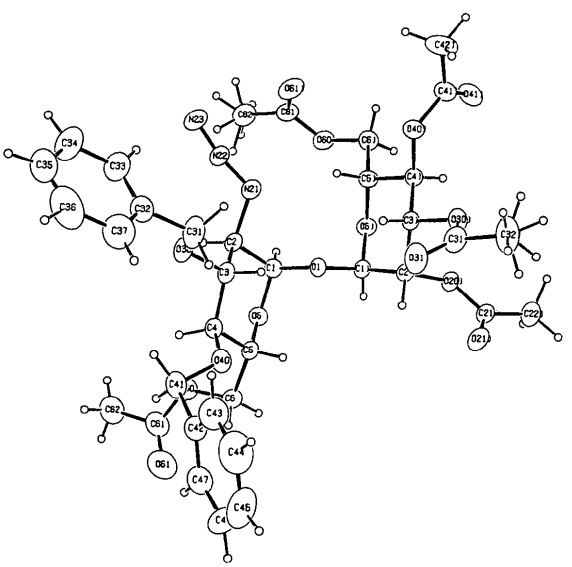


Fig. 1. Molecular model of the title compound (*ORTEP* II, Johnson, 1970).

Table 2. *A selection of the most relevant bond angles* (°) *and torsion angles* (°), *with e.s.d.'s in parentheses*

Full tables have been deposited.

| | | | |
|---|---|---|---|
| O(5)–C(1)–C(2) | 110·1 (5) | O(5)–C(1)–O(1) | 112·6 (5) |
| C(2)–C(1)–O(1) | 104·8 (5) | C(1)–C(2)–C(3) | 109·8 (5) |
| C(2)–C(3)–C(4) | 111·6 (6) | C(3)–C(4)–C(5) | 112·7 (5) |
| C(4)–C(5)–O(5) | 113·4 (4) | C(4)–C(5)–C(6) | 113·7 (5) |
| O(5)–C(5)–C(6) | 107·8 (6) | C(1)–O(5)–C(5) | 115·7 (5) |
| N(21)–N(22)–N(23) | 170·4 (8) | C(1)–O(1)–C(1′) | 115·7 (5) |
| O(1)–C(1′)–C(2′) | 104·5 (5) | O(5′)–C(1′)–O(1) | 112·5 (4) |
| O(5′)–C(1′)–C(2′) | 112·5 (5) | C(1′)–C(2′)–C(3′) | 109·4 (4) |
| C(2′)–C(3′)–C(4′) | 111·4 (5) | C(3′)–C(4′)–C(5′) | 109·0 (5) |
| C(4′)–C(5′)–O(5′) | 109·4 (4) | C(4′)–C(5′)–C(6′) | 114·3 (5) |
| O(5′)–C(5′)–C(6′) | 105·6 (5) | C(5′)–O(5′)–C(1′) | 113·2 (4) |

| | |
|---|---|
| C(1)–C(2)–C(3)–C(4) | −53·7 (7) |
| C(2)–C(3)–C(4)–C(5) | 45·6 (7) |
| C(3)–C(4)–C(5)–O(5) | −42·7 (7) |
| C(4)–C(5)–O(5)–C(1) | 51·0 (6) |
| C(5)–O(5)–C(1)–C(2) | −59·4 (6) |
| O(5)–C(1)–C(2)–C(3) | 59·8 (7) |
| C(1′)–C(2′)–C(3′)–C(4′) | −51·4 (6) |
| C(2′)–C(3′)–C(4′)–C(5′) | 56·2 (6) |
| C(3′)–C(4′)–C(5′)–O(5′) | −59·5 (6) |
| C(4′)–C(5′)–O(5′)–C(1′) | 61·5 (6) |
| C(5′)–O(5′)–C(1′)–C(2′) | −57·9 (6) |
| O(5′)–C(1′)–C(2′)–C(3′) | 51·4 (6) |
| N(22)–N(21)–C(2)–C(1) | 151·0 (7) |
| N(22)–N(21)–C(2)–H(2) | 34·0 (4) |
| C(33)–C(32)–C(31)–O(30) | −58·5 (12) |
| O(60)–C(6)–C(5)–O(5) | −62·0 (7) |
| O(60)–C(6)–C(5)–C(4) | 64·5 (8) |
| O(60′)–C(6′)–C(5′)–O(5′) | 67·9 (6) |
| O(60′)–C(6′)–C(5′)–C(4′) | −171·8 (5) |

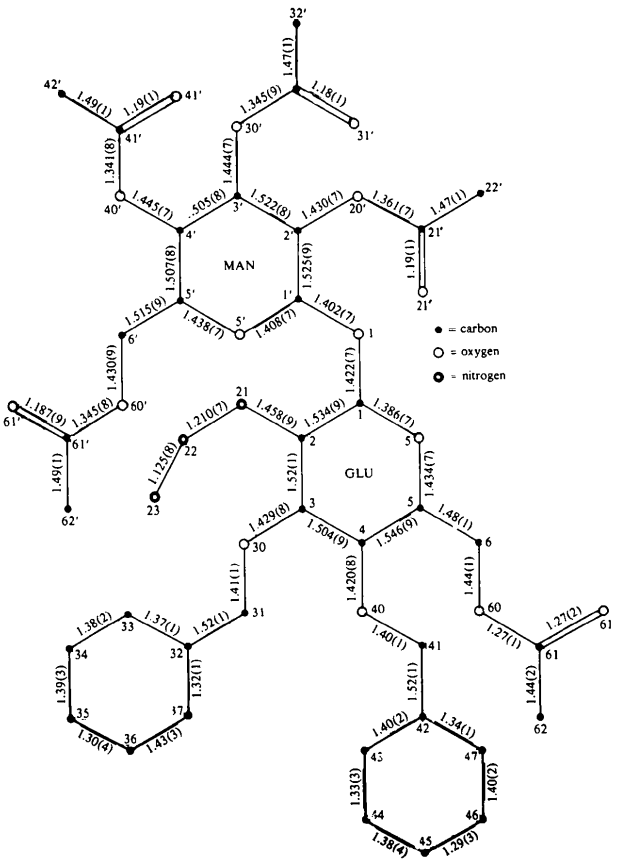



Fig. 2. Atom-numbering scheme and bond lengths (Å) with e.s.d.'s in parentheses.

direction of a $^2H_1$ form. The larger distortion for the glucopyranosyl ring may possibly be caused by the large *O*-benzyl substituents attached to C(3) and C(4).

Bond lengths and a selection of bond angles and torsion angles* are given in Fig. 2 and Table 2, respectively.

All bonding data of the benzyl and acetyl substituents are in the normal range [with the exception of the less accurate gluco C(6) group] and need no further discussion. This also holds for the azido group. The bond lengths of 1·210 Å for N(21)–N(22) and 1·125 Å for N(22)–N(23) and the significantly non-linear angle N(21)–N(22)–N(23) of 170·4° agree well with the results of MO calculations on that group (Patai, 1971) and our previous investigations on azido-substituted carbohydrates (Luger & Paulsen, 1974, 1976; Schmidt, Luger & Paulsen, 1980).

In the pyranosyl ring the C–C bond lengths and angles are in the normal range for carbohydrates (Foces-Foces, Cano & García-Blanco, 1980). The exo- and endocyclic C–O bond lengths at C(1) and C(1′) are of special interest. Since both monosaccharide fragments belong to the $\alpha$ series the anomeric effect should have an influence in that the C(1)–O(5) bonds in both rings should be shortened. Indeed, we find for the *gluco* as well as for the *manno* pyranosyl ring that this bond is shorter by 6·9$\sigma$ (*gluco*) and 4·3$\sigma$ (*manno*) than the corresponding O(5)–C(5) bonds.

In Table 3 the C–O bonding data are shown for this structure and for the other trehalose derivatives known so far. The mean values suggest that all C(1)–O bonds are alike and 0·2 Å shorter than the C(5)–O bonds. The bond angles show a tendency for $\beta$ and $\delta$ to be smaller by 2–3° than $\alpha$, $\gamma$ and $\varepsilon$. The disaccharides of trehalose type contain a characteristic C–O–C–O–C–O–C sequence, whereas oligosaccharides which are not linked *via* their anomeric centres or, for instance, methyl pyranosides only have a C–O–C–O–C–*R* sequence with $R \neq OR'$. Nevertheless, a comparison with mean C–O bonds, calculated for these types of structures (Table 3), and with data derived from *ab initio* molecular-orbital calculations for the model compound dimethoxymethane (Jeffrey, Pople, Binkley & Vishveshwara, 1978) confirms the tendency stated above.

The relative conformation of the two monosaccharide components is given by the torsion angles around the glycosidic bonds. Usually, the con-

* See previous footnote.

Table 3. *Comparison of various X-ray data (bond lengths in* Å, *angles in* deg) *for the sequence* C(5)–O(5)–C(1)–O(1)–C(1′)–O(5′)–C(5′) (α, β, γ, δ, ε)

| Compound | Reference | C(5)–O(5) | O(5)–C(1) | C(1)–O(1) | O(1)–C(1′) | C(1′)–O(5′) | O(5′)–C(5′) |
|---|---|---|---|---|---|---|---|
| Mannotrehalose | (*e*) | 1·434 | 1·386 | 1·422 | 1·402 | 1·408 | 1·438 |
| Trehalose dihydrate | (*a*) | 1·437 | 1·423 | 1·417 | 1·421 | 1·407 | 1·424 |
| Trehalose dihydrate | (*b*) | 1·433 | 1·421 | 1·415 | 1·422 | 1·404 | 1·431 |
| Trehalose.CaBr | (*c*) | 1·454 | 1·423 | 1·406 | 1·406* | 1·423* | 1·454* |
| Mean | | 1·440 (10) | 1·413 (18) | 1·415 (7) | 1·413 (10) | 1·411 (9) | 1·437 (13) |
| Methyl α-pyranosides (mean) | (*d*) | 1·435 (9) | 1·416 (3) | 1·404 (7) | | | |
| α-Glycosidic linkages (mean) | (*d*) | 1·434 (4) | 1·418 (7) | 1·408 (12) | | | |
| Theoretical | (*d*) | 1·444 | 1·423 | 1·423 | | | |
| | | α | β | γ | δ | ε | |
| Mannotrehalose | (*e*) | 115·7 | 112·6 | 115·7 | 112·5 | 113·2 | |
| Trehalose dihydrate | (*a*) | 114·1 | 111·9 | 115·7 | 111·3 | 114·3 | |
| Trehalose dihydrate | (*b*) | 114·0 | 112·1 | 115·8 | 111·7 | 114·2 | |
| Trehalose.CaBr | (*c*) | 113·5 | 110·9 | 113·2 | 110·9* | 113·5* | |
| Mean | | 114·3 (10) | 111·9 (7) | 115·1 (13) | 111·6 (7) | 113·8 (5) | |
| Methyl α-pyranosides | (*d*) | 113·4 (9) | 112·3 (5) | 113·1 (2) | | | |
| α-Glycosidic linkages (mean) | (*d*) | 114·1 (6) | 111·2 (8) | 115·0 (31) | | | |
| Theoretical | (*d*) | 115·9 | 113·9 | 115·9 | | | |

References: (*a*) Taga, Senma & Osaki (1972); (*b*) Brown, Rohrer, Berking, Beevers, Gould & Simpson (1972); (*c*) Cook & Bugg (1973); (*d*) Jeffrey, Pople, Binkley & Vishveshwara (1978); (*e*) this work.

* Primed values are equal to unprimed ones because of symmetry.

formational angles $\varphi$ = H(1)–C(1)–O(1)–C(1′) and $\psi$ = C(1)–O(1)–C(1′)–H(1′) are considered (Sundararajan & Rao, 1969); however, because of the uncertainty of the H positions derived from X-ray diffraction, the use of the angles $\varphi_1$, $\varphi_2$, $\psi_1$, $\psi_2$ (Sundaralingam, 1968), as defined in Fig. 3, seems to be more appropriate. Fig. 3 shows that C atom 1 of one residue is almost *trans* with respect to C atom 2 of the opposite residue and in a *gauche* position to the opposite ring O atom. All three trehalose structures agree well in this respect, their $\varphi$ and $\psi$ torsion angles differing at most by 15°. This conformation corresponds to that of a twofold axis through the bridge oxygen atom O(1), which is realized exactly in the CaBr derivative as a consequence of the crystal symmetry, and is realized in good approximation for the two other structures. This result is noteworthy and could not be expected originally, since the three trehalose compounds have totally different structural properties: in trehalose dihydrate the two residues are connected by hydrogen bonding *via* two water molecules; in the calcium bromide structure the $Ca^{2+}$ ion plays an important role in being coordinated to six hydroxyl O atoms of glucose residues, and hydrogen bonds are also present; finally, in the mannotrehalose derivative one residue has a *manno* instead of a *gluco* configuration and the molecule is highly substituted, totally lacking hydrogen bonds. Nevertheless, none of these influences seems to be important for the conformation around the glycosidic bonds and it seems that the twofold-axis arrangement is a special property and very stable for the α,α(1→1) glycosidic linkage. It

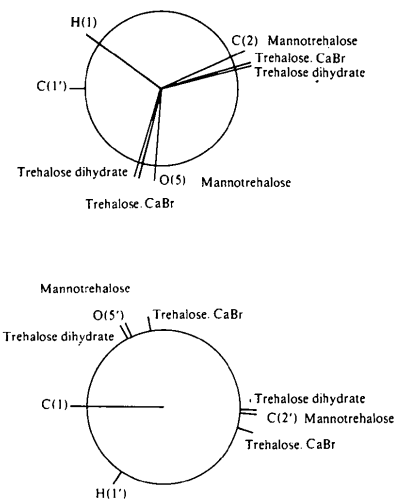



Fig. 3. Conformational situation along the glycosidic bonds C(1)–O(1) (above) and O(1)–C(1′) (below). According to Sundaralingam (1968), the torsion angles are defined as $\varphi_1$ = O(5)–C(1)–O(1)–C(1′), $\varphi_2$ = C(2)–C(1)–O(1)–C(1′), $\psi_1$ = C(1)–O(1)–C(1′)–O(5′), $\psi_2$ = C(1)–O(1)–C(1′)–C(2′). Actual values (°) for the three trehalose structures (in the sequence trehalose dihydrate, trehalose.CaBr, mannotrehalose) are $\varphi_1$ = 74·9, 76·9, 85·9; $\varphi_2$ = −165·3, −163·5, −154·5; $\psi_1$ = 61·7, 76·9, 62·8; $\psi_2$ = −177·5, −163·5, −174·8.

should be noted that for other types of linkages the conformational variety is larger. For instance, in disaccharides of maltose and cellobiose type, having α(1→4) and β(1→4) linkages, the conformational angles vary over a range of more than 30° (Kanters, Gaykema & Roelofsen, 1978).

The arrangement of the large substituents can be described by appropriate torsion angles. The orientation of the azido group at C(2) is determined by its steric interaction with the phenyl ring of the 3-benzyl group and the 6′-acetate group. In the adopted position with an almost 30° deviation from a *trans–gauche* arrangement with respect to C(1) and C(3) [torsion angle N(22)–N(21)–C(2)–H(2) = +34 (4)°] the azido group has close intramolecular C···H contacts [N(23)···H(33) = 2·59, N(21)···H(5′) = 2·42 Å] and its approach to the 6′-acetate group [N(22)···O(61′) = 3·101 Å] is just above the van der Waals distance.

As expected, the acetate groups at the mannopyranosyl ring (2-OAc, 3-OAc, 4-OAc) are positioned with their C=O groups almost synparallel to the corresponding C(ring)–H bond. The arrangement of the *O*-benzyl groups at C(3) and C(4) relative to the glucopyranosyl ring is, however, totally different from that of either the acetyl or the benzoyl groups. With respect to the bond O(*i*0)–C(*i*1) (*i* = 3, 4), which is almost synparallel to the corresponding ring C–H bond, the phenyl rings are markedly inclined, as the torsion angles C(33)–C(32)–C(31)–O(30) = −58 (1) and C(43)–C(42)–C(41)–O(40) = +79 (1)° show. In this arrangement these two groups need a large volume in the direction of the vicinal substituents, which may be the source of the larger distortion of the glucopyranosyl ring. For the substituents at C(6) and C(6′) the same discrepancies in their conformation are found as in trehalose dihydrate. Similarly as in that structure, the C(6)–O(60) bond has the *gauche–gauche* conformation while the C(6′)–O(60′) bond is *gauche–trans* with respect to O(5′) and C(4′). In the CaBr trehalose derivative the conformation, which has to be equal in both cases for symmetry reasons, is *gauche–trans*.

The molecular packing in the crystal lattice (Fig. 4) is determined by van der Waals forces. There is only one intermolecular contact distance below 3·2 Å: C(6)···O(61′) = 3·025 (9) Å with the symmetry operation $2-x, -\frac{1}{2}-y, \frac{1}{2}-z$ for O(61′). The packing ratio (Foces-Foces, Cano & García-Blanco, 1980), which is the ratio of cell volume/number of non-hydrogen atoms, is 18·8 Å$^3$. For trehalose dihydrate it is 16·6 Å$^3$. Both values follow the rule that for structures lacking hydrogen bonds this ratio should be enlarged by about 2 Å$^3$.

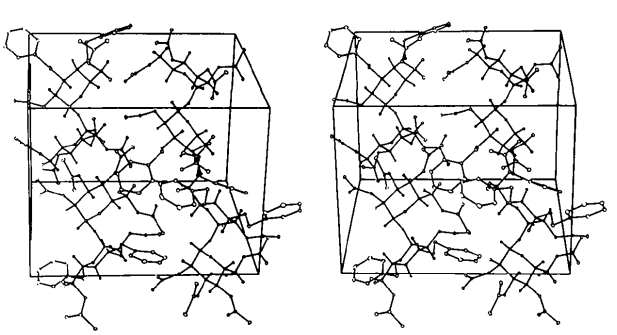


Fig. 4. The unit cell projected down **a** (approximately, 25° rotation about **b**); **b** runs across the page, **c** points upward (*ORTEP* II, Johnson, 1970).

## References


ARCAMONE, F. & BIZIOLI, F. (1957). *Gazz. Chim. Ital.* **87**, 896–902.

BROWN, G. M., ROHRER, D. C., BERKING, B., BEEVERS, C. A., GOULD, R. D. & SIMPSON, R. (1972). *Acta Cryst.* B**28**, 3145–3158.

COOK, W. J. & BUGG, C. E. (1973). *Carbohydr. Res.* **31**, 265–275.

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, S. (1980). *Acta Cryst.* B**36**, 377–384.

HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.

JEFFREY, G. A., POPLE, J. A., BINKLEY, J. S. & VISHVESHWARA, S. (1978). *J. Am. Chem. Soc.* **100**, 373–379.

JEFFREY, G. A. & YATES, J. H. (1979). *Carbohydr. Res.* **74**, 319–322.

JOHNSON, C. K. (1970). *ORTEP* II. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KANTERS, J. A., GAYKEMA, W. P. J. & ROELOFSEN, G. (1978). *Acta Cryst.* B**34**, 1873–1881.

KOTHE, G., LUGER, P. & PAULSEN, H. (1976). *Acta Cryst.* B**32**, 2710–2712.

KOTHE, G., LUGER, P. & PAULSEN, H. (1979). *Acta Cryst.* B**35**, 2079–2087.

LEUNG, F., CHANZY, H. D., PÉREZ, S. & MARCHESSAULT, R. H. (1976). *Can. J. Chem.* **54**, 1365–1371.

LUGER, P. & PAULSEN, H. (1974). *Chem. Ber.* **107**, 1579–1589.

LUGER, P. & PAULSEN, H. (1976). *Acta Cryst.* B**32**, 2774–2779.

MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1975). *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.

PATAI, S. (1971). *The Chemistry of the Azido Group.* London: Interscience.

PAULSEN, H. & SUMFLETH, B. (1979). *Chem. Ber.* **112**, 3203–3213.

SCHMIDT, H. J., LUGER, P. & PAULSEN, H. (1980). *Acta Cryst.* B**36**, 2646–2650.

STEWART, J. M., MACHIN, P. A., AMMON, H. L., DICKINSON, C., HECK, H. & FLACK, H. (1976). The XRAY system – version of March 1976. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

SUNDARALINGAM, M. (1968). *Biopolymers*, **6**, 189–213.

SUNDARARAJAN, P. R. & RAO, V. S. R. (1969). *Biopolymers*, **8**, 313–323.

TAGA, T., SENMA, M. & OSAKI, K. (1972). *Acta Cryst.* B**28**, 3258–3263.

UMEZAWA, S. (1974). *Adv. Carbohydr. Chem. Biochem.* **30**, 137.