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Structure of 2,4-Diazido-2,4-dideoxy-1,6-anhydro-β-D-glucopyranose

BY HEINZ-JÜRGEN SCHMIDT AND 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*

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Abstract

Since NMR investigations of 2,4-diazido-2,4-dideoxy-1,6-anhydro-β-D-glucopyranose, $C_6H_8N_6O_3$, indicate that the molecule in solution prefers the unusual $^2S_0$ conformation, an investigtion of the crystalline state was made by X-ray analysis. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 24{\cdot}010\,(7)$, $b = 8{\cdot}539\,(4)$, $c = 8{\cdot}580\,(4)$ Å, $Z = 8$. 1831 diffractometer data were refined to an R value of 4·3%. In the crystal the molecule was found to have a distorted $^1C_4$ conformation similar to those of other 1,6-anhydropyranoses previously investigated. The 1,3-diaxial repulsions of the azido groups have minor influence on the molecular geometry. The middle N atoms of both azido groups have short contacts to a pyranosyl ring O atom. One (intramolecular) contact distance is about 2·8 Å, the other (intermolecular) is 2·9 Å.

Introduction

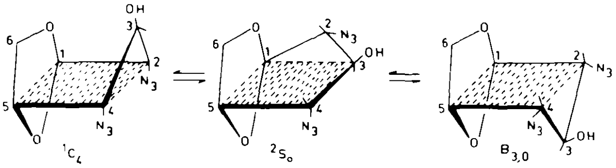
A number of anhydro sugars have been studied by X-ray methods. The system investigated most frequently is that of 1,6-anhydroglycopyranose of which examples of the *altro* (Brown & Thiessen, 1969), *gluco* (Park, Kim & Jeffrey, 1971), *gulo* (Berking & Seeman, 1971), *talo* (Panagiotopoulos, 1974), *galacto* (Foces-Foces, Cano & García-Blanco, 1976) and *manno* (Hecht, Luger & Reinhardt, 1977) configurations are known.

A comparison of those investigations shows that all the molecules have almost the same structure with a slightly distorted $^1C_4$ chair conformation of the pyranosyl ring. Compared to an ideal chair form the ring is flattened at C(3) (the most flexible part of the molecule) causing the distances O(2)—O(4) and O(3)—C(6) to be lengthened. These distortions are a consequence of the formation of the anhydro bridge, *i.e.* the fusion to the five-membered ring.

In the field of conformational analysis the 1,6-anhydro-*gluco* configuration is of special interest since in the $^1C_4$ conformation 1,3-diaxial interactions occur twice in the molecule.

NMR spectra taken from 3-amino-3-deoxy-1,6-anhydro-β-D-glucopyranose and its ammonium salt (Trnka, Cerny, Budesinsky & Pacek, 1975) were interpreted by assuming that the pyranosyl ring is distorted to the skew conformation in solution. However, the X-ray structure determinations of both compounds (Noordik & Jeffrey, 1977; Małuszyńska, Takagi & Jeffrey, 1977) showed that in both cases a $^1C_4$ chair conformation similar to that of 1,6-anhydro-β-D-glucopyranose itself is present.

We observed coupling constants in the NMR spectra of 2,4-diazido-2,4-dideoxy-1,6-anhydro-β-D-glucopyranose (I) and 2,4-diammonio-2,4-dideoxy-1,6-anhydro-β-D-glucopyranose which indicate a conformational difference (Paulsen & Koebernick, 1976). For the diazido compound a $^2S_0$ conformation (II) was predominant in solution whereas the diammonium compound should be almost completely in a $B_{3,0}$ boat conformation.* These conformational differences are likely to be a consequence of the strong 1,3-diaxial interactions caused by the substituents at C(2) and C(4). In fact, it was found in the idopyranose system



(I) (II) (III)

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* Note that in our previous paper (Paulsen & Koebernick, 1976) a different nomenclature was used. The symbols used in this paper seem to be more appropriate and correspond to the IUPAC rules.

that the 1,3-diaxial interactions are larger for two *syn*-diaxial azido groups than, for instance, for two acetoxy groups. In the case of the diammonium compound it seems reasonable that the electrostatic repulsions cause the two positively charged ammonium groups to be separated as much as possible. This is realized in a $B_{3,0}$ boat conformation (III). Here we report the structure determination of the diazido compound. It was not possible to obtain crystals of the diammonium compound.

Experimental

Colourless crystals of 2,4-diazido-2,4-dideoxy-1,6-anhydro-β-D-glucopyranose (AZOSE) become yellowish and decompose slowly when exposed to X-rays. Preliminary lattice constants and the space group were determined from oscillation and Weissenberg photographs. Precise cell parameters (from high-order axial reflections) and 1831 three-dimensional intensity data of an octant (h,k,l all positive) were measured on a DEC PDP 15 computer-controlled Siemens diffractometer with Zr-filtered Mo $K\alpha$ radiation (λ = 0·71069 Å) using the ω–2θ scan mode. The chosen crystal had an approximate size 0·55 × 0·52 × 0·43 mm. Two reference reflections were used for control and scaling of a small decrease of the intensities (up to 15% at the end of the measurement) in the course of the data collection. The most relevant crystallographic data are given in Table 1. The phase problem was solved by direct methods with the *MULTAN* program (Main, Woolfson & Germain, 1975). 200 reflections with $|E| > 1\cdot5$ and six reflections in the starting set were used to determine the structure.

The atom parameters were refined by least-squares methods, using anisotropic temperature factors for the heavy atoms and isotropic temperature factors for the hydrogens. As long as isotropic temperature factors were used, full-matrix refinement was applied. With anisotropic temperature factors, the matrix was subdivided into two blocks, each associated with the parameters of one independent molecule. The final R value $\{R = \sum_{\mathbf{h}} [|F_o(\mathbf{h})| - |F_c(\mathbf{h})|]/\sum_{\mathbf{h}} |F_o(\mathbf{h})|\}$ was 0·043. All observed reflections were given unit weights. Scattering factors implemented in the corresponding routine of the XRAY 76 system were used. The refinement and related calculations were performed on a CDC Cyber 175 computer (Wissenschaftliches Rechenzentrum Berlin) using the XRAY 76 system (Stewart, Machin, Ammon, Dickinson, Heck & Flack, 1976). The atomic parameters are given in Table 2.*

Table 1. *Crystal data of* 2,4-*diazido*-2,4-*dideoxy*-1,6-*anhydro*-β-D-*glucopyranose* (*AZOSE*)

$C_6H_8N_6O_3$, $M_r = 212\cdot2$
Orthorhombic, space group $P2_12_12_1$
Unit-cell dimensions
$a = 24\cdot010\ (7)$ Å
$b = 8\cdot539\ (4)$
$c = 8\cdot580\ (4)$
$V_c = 1759\cdot1$ Å^3
$D_x = 1\cdot61$ Mg m^{-3}
$Z = 8$
Number of reflections: 1831 ($2° \le \theta \le 26°$)
Number of unobserved reflections ($I < 2\sigma$): 128

Molecular geometry

A stereoview of the molecule is given in Fig. 1 (Johnson, 1970). The bond lengths and valence angles are given in Tables 3 and 4; the torsion angles and

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* Lists of structure factors, thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35345 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional coordinates with e.s.d.'s in parentheses*

	Molecule (1)			Molecule (2)		
	x	y	z	x	y	z
C(1)	0·7453 (2)	0·7078 (6)	0·1515 (5)	0·4918 (2)	0·8828 (5)	0·5429 (5)
C(2)	0·8002 (2)	0·7719 (5)	0·2107 (5)	0·5489 (2)	0·9260 (5)	0·4790 (5)
C(3)	0·7931 (2)	0·8650 (5)	0·3648 (5)	0·5484 (2)	1·0793 (5)	0·3863 (5)
C(4)	0·7452 (2)	0·8018 (5)	0·4663 (5)	0·5041 (2)	1·1964 (5)	0·4456 (5)
C(5)	0·6977 (2)	0·7353 (5)	0·3696 (5)	0·4525 (2)	1·1139 (5)	0·5076 (5)
C(6)	0·6732 (2)	0·8501 (6)	0·2540 (6)	0·4252 (2)	1·0023 (6)	0·3916 (6)
O(3)	0·7824 (2)	1·0229 (3)	0·3189 (4)	0·5383 (1)	1·0385 (4)	0·2274 (3)
O(5)	0·7194 (1)	0·6163 (4)	0·2667 (4)	0·4694 (1)	1·0075 (4)	0·6288 (3)
O(1)	0·7085 (1)	0·8324 (4)	0·1184 (4)	0·4548 (2)	0·8562 (4)	0·4145 (4)
N(21)	0·8442 (2)	0·6504 (5)	0·2270 (7)	0·5929 (2)	0·9276 (6)	0·6004 (5)
N(22)	0·8313 (2)	0·5205 (5)	0·2761 (5)	0·5807 (2)	0·9780 (5)	0·7303 (5)
N(23)	0·8283 (2)	0·3958 (6)	0·3188 (7)	0·5768 (2)	1·0193 (7)	0·8548 (5)
N(41)	0·7659 (2)	0·6695 (5)	0·5628 (4)	0·5267 (2)	1·2875 (5)	0·5776 (4)
N(42)	0·7937 (2)	0·7082 (5)	0·6775 (5)	0·5491 (2)	1·4127 (5)	0·5405 (4)
N(43)	0·8193 (2)	0·7270 (6)	0·7862 (6)	0·5692 (2)	1·5298 (6)	0·5226 (5)

numbering scheme are given in Fig. 2 with the corresponding data of 1,6-anhydro-β-D-glucopyranose (Park, Kim & Jeffrey, 1971). Since the bond lengths and angles of the two molecules in the asymmetric unit do not differ significantly, the following discussion is based on the mean values.

The pyranose ring has the $^1C_4$ chair conformation, whereas in solution we found it to be in a skew conformation (Paulsen & Koebernick, 1976). The chair is strained in a way similar to the other 1,6-anhydropyranoses (*cf.* data given in Tables 3 and 4 and in Fig. 2). The torsion angles at C(3) [C(1)–C(2)–C(3)–C(4) = 31·0, C(2)–C(3)–C(4)–C(5) = −32·6°] are less than half those of the angles at the opposite atom O(5). The distances of C(3) and O(5) from the least-squares plane through C(1), C(2), C(4), C(5) are very different. The distance of C(3) from that plane is 0·42 Å, and that of O(5) is 0·83 Å. These data show that the chair is flattened at C(3) and tends to have an envelope conformation. Since the structure of 1,6-anhydro-β-D-glucopyranose has almost the same properties, it can be concluded that the straining of the chair is mainly a consequence of the five-membered-ring fusion (anti-reflex effect). Compared with this effect the repulsion of the azido groups has little influence on the chair distortion. This can be seen when comparing the torsion angles at C(3) of the azido compound with corresponding angles in 1,6-anhydroglucose: in the azido compound the angles C(1)–C(2)–C(3)–C(4) and C(2)–C(3)–C(4)–C(5) are 4·2 and 2·6° smaller, respectively, than the corresponding angles in the gluco compound. In contrast, the differences of the torsion

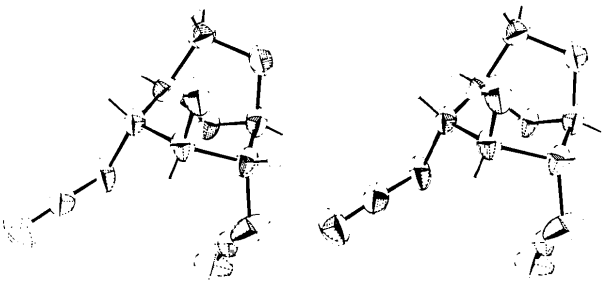


Fig. 1. Molecular model of 2,4-diazido-2,4-dideoxy-1,6-anhydro-β-D-glucopyranose (*ORTEP* II, Johnson, 1970).

Table 3. *Bond lengths* (Å) *in molecules* (1) *and* (2) *of AZOSE* (*e.s.d.'s in parentheses*) *and in* 1,6-*anhydro-β*-D-*glucopyranose*

	AZOSE Molecule (1)	AZOSE Molecule (2)	1,6-Anhydro-β-D-gluco-pyranose
C(1)–C(2)	1·512 (7)	1·521 (7)	1·521
C(2)–C(3)	1·552 (6)	1·532 (6)	1·538
C(3)–C(4)	1·538 (6)	1·545 (6)	1·538
C(4)–C(5)	1·517 (7)	1·518 (6)	1·519
C(5)–C(6)	1·513 (7)	1·525 (7)	1·525
C(6)–O(1)	1·445 (6)	1·447 (6)	1·445
C(1)–O(1)	1·411 (6)	1·433 (6)	1·430
C(1)–O(5)	1·404 (6)	1·401 (5)	1·402
C(5)–O(5)	1·442 (5)	1·439 (5)	1·444
C(3)–O(3)	1·428 (5)	1·428 (5)	1·425
C(2)–N(21)	1·486 (7)	1·481 (6)	
N(21)–N(22)	1·225 (7)	1·229 (6)	
N(22)–N(23)	1·129 (7)	1·129 (6)	
C(4)–N(41)	1·486 (6)	1·477 (6)	
N(41)–N(42)	1·233 (6)	1·237 (6)	
N(42)–N(43)	1·127 (7)	1·121 (6)	

Table 4. *Bond angles* (°) *in molecules* (1) *and* (2) *of AZOSE* (*e.s.d.'s in parentheses*) *and in* 1,6-*anhydro-β*-D-*glucopyranose*

	AZOSE Molecule (1)	AZOSE Molecule (2)	1,6-Anhydro-β-D-gluco-pyranose
O(5)–C(1)–C(2)	110·4 (4)	110·5 (4)	110·0
O(1)–C(1)–C(2)	109·8 (4)	108·6 (3)	110·5
O(1)–C(1)–O(5)	106·6 (4)	106·7 (4)	105·8
C(1)–C(2)–C(3)	112·1 (4)	112·8 (4)	111·7
C(2)–C(3)–C(4)	112·6 (4)	112·8 (4)	112·4
C(3)–C(4)–C(5)	112·4 (4)	112·1 (4)	111·7
C(4)–C(5)–O(5)	109·1 (4)	108·4 (4)	109·6
C(5)–O(5)–C(1)	101·5 (3)	102·0 (3)	102·0
C(4)–C(5)–C(6)	114·0 (4)	114·2 (4)	112·5
O(5)–C(5)–C(6)	101·2 (4)	101·4 (4)	101·5
C(5)–C(6)–O(1)	103·5 (4)	103·9 (4)	103·1
C(6)–O(1)–C(1)	106·4 (3)	105·7 (4)	106·8
C(2)–C(3)–O(3)	105·6 (3)	106·8 (3)	107·9
C(4)–C(3)–O(3)	110·7 (4)	110·8 (4)	110·6
C(1)–C(2)–N(21)	113·4 (4)	112·9 (4)	
C(3)–C(2)–N(21)	110·8 (4)	111·3 (4)	
C(3)–C(4)–N(41)	109·4 (4)	109·9 (4)	
C(5)–C(4)–N(41)	105·7 (4)	106·0 (3)	
C(2)–N(21)–N(22)	119·0 (4)	118·2 (4)	
N(21)–N(22)–N(23)	169·0 (5)	170·7 (5)	
C(4)–N(41)–N(42)	115·0 (4)	114·6 (4)	
N(41)–N(42)–N(43)	172·6 (5)	172·9 (5)	

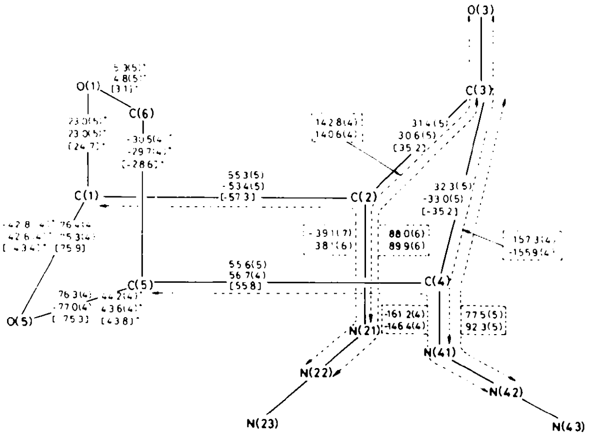


Fig. 2. Torsion angles (°) in the bicyclic ring system. Upper and lower values correspond to molecules (1) and (2) respectively, values given in square brackets are from 1,6-anhydro-β-D-glucopyranose. An asterisk indicates torsion angles of the five-membered ring.

angles at O(5) are negligible. Thus, the *syn*-diaxial interaction intensifies the flattening of the chair, but this effect is not as great as expected from the results found in solution. This becomes reasonable if the contact distance of N(21) and N(41) is considered. The distortion of the chair causes this distance to be 3·45 Å whereas the sum of two van der Waals radii of nitrogen is only 3·10 Å (Bondi, 1964).

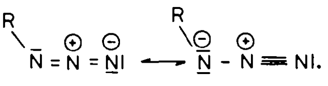
The geometry of a pyranose ring can be characterized in an exact manner by ring-puckering parameters, calculated by the method of Cremer & Pople (1975). The parameters of AZOSE are θ = 151·45 (151·37), φ = 177·86° (173·95°), q_2 = 0·292 (0·292), q_3 = −0·537 (−0·535) and Q = 0·612 Å (0·609 Å) (Jeffrey & Yates, 1979), with the corresponding values for molecule (2) given in parentheses. The total puckering is the same as in 1,6-anhydro-β-D-glucopyranose (0·610 Å) and the θ and φ values show that the type of distortion is similar to that of the other anhydro compounds.

The five-membered anhydro ring is the least flexible part of the molecule. As in the other 1,6-anhydro sugars the ring has a distorted E^0 conformation with O(5) lying 0·62 Å above the plane through C(1), O(1), C(6), C(5). The distortion is expressed by a non-zero torsion angle C(5)–C(6)–O(1)–C(1) = 5·1°.

In the segment C(6)–O(1)–C(1)–O(5)–C(5) the distances O(1)–C(1) and O(5)–C(1) are shorter than the other C–O distances (*cf.* Table 3). This is a consequence of the anomeric effect (Jeffrey, Pople & Radom, 1972, 1974; Jeffrey, Pople, Binkley & Vishveshwara, 1978). There is a difference in length between the C(1)–O(1) (1·411 and 1·433 Å) and C(1)–O(5) bonds (1·404 and 1·401 Å). Although this difference is small, a similar difference has been found in all 1,6-anhydropyranoses investigated. For pyranoses and pyranosides the anomeric effect is rationalized mainly by a dipole–dipole interaction, whereas the contributions of a back donation and a steric term are of minor influence in this case (Jeffrey, Pople & Radom, 1972). The back donation results from the overlap of an O p orbital with the σ^* orbital of a neighbouring C–O bond (Romers, Altona, Buys & Havinga, 1969). It is of note that, due to the different torsion angles found along the bonds C(1)–O(5) [O(1)–C(1)–O(5)–C(5) = −42·7°] and C(1)–O(1) [O(5)–C(1)–O(1)–C(6) = 23·0°], the overlap of the O(5) p orbital with the C(1)–O(1) σ^* orbital should be greater than the overlap of the O(1) p orbital with the C(1)–O(5) σ^* orbital. The bond lengths cited above are consistent with this interpretation.

The azido groups

The azido group can be represented as shown below:



The bond lengths of 1·231 Å for N(1)–N(2) and 1·127 Å for N(2)–N(3) (average values of both groups) agree with MO calculations (Patai, 1971), data from microwave spectra (Salathiel & Curl, 1965) and results of our previous investigations (Paulsen, Györgydeak & Friedmann, 1974*a*,*b*; Luger & Paulsen, 1974, 1976). They indicate that (II) is more dominant. The anomeric and *exo*-anomeric effect, as well as the 1,3-diaxial repulsion of the azido group, can be explained by the negative charge at N(1).

The torsion angles of the C–N bonds show the orientation of the azido groups. It can be seen that the group at C(2) points below the six-membered ring (Fig. 1). The contact distance between the central N(2) atom and the ring O(5) atom is 2·806 (5) Å [2·818 (5) Å]. The corresponding group at C(4) points away from the molecule, and the central N(42) atom also approaches a ring O(5′) atom of a symmetry-related molecule [symmetry operation $\frac{3}{2} - x$, $1 - y$, $\frac{1}{2} + z$ for molecule (1), $1 - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$ for molecule (2)] with a contact distance of 2·891 (5) Å [2·983 (5) Å]. The intramolecular contact distances in particular are shorter than the sum of the van der Waals radii which is 3·07 Å (Bondi, 1964). The orientation of the azido groups, the short N···O distance and the fact that the middle N has a positive partial charge suggest that there is an additional electrostatic attraction between the middle N and the lone electron pairs of the O, which stabilizes this orientation.

The crystal packing

The packing of the molecules (Fig. 3) shows that the azido groups at C(4) line up to form a chain-like arrangement. The group in one molecule (1) points towards the ring oxygen of another molecule (1) related by the symmetry operation $\frac{3}{2} - x$, $1 - y$, $\frac{1}{2} + z$. In turn,

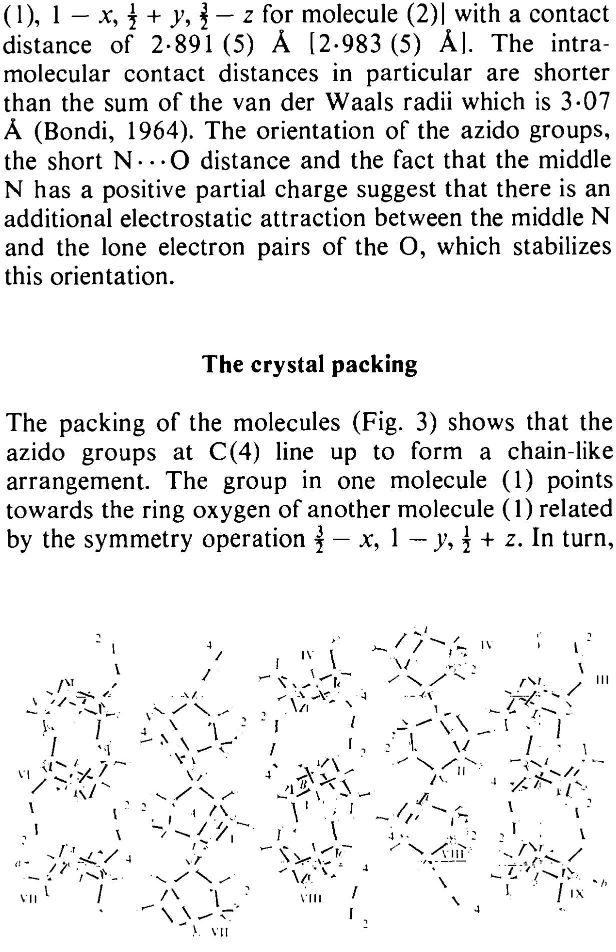


Fig. 3. Projection of the unit cell on the *ac* plane. Molecules (1) and (2) of the asymmetric unit are marked by *A* and *B*. Symmetry operations are (I) x,y,z; (II) $-\frac{1}{2} + x$, $\frac{3}{2} - y$, $1 - z$; (III) $\frac{1}{2} - x$, $1 - y$, $\frac{1}{2} + z$; (IV) $1 - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$; (V) $\frac{3}{2} - x$, $1 - y$, $\frac{1}{2} + z$; (VI) $\frac{1}{2} + x$, $\frac{3}{2} - y$, $1 - z$; (VII) $\frac{3}{2} - x$, $1 - y$, $-\frac{1}{2} + z$; (VIII) $1 - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$; (IX) $\frac{1}{2} - x$, $1 - y$, $-\frac{1}{2} + z$. The numbers 2 and 4 indicate the azido groups at C(2) and C(4).

the group at C(4) of this molecule points towards the O of the neighbour ($x, y, z + 1$). There is a second similar chain in the other half of the cell running in the opposite direction. For the C(4) azido groups of molecules (2) there is a similar system: the C(4) group points towards another molecule (2) ($1 - x, \frac{1}{2} + y, \frac{3}{2} - z$), and its azido group points towards the next neighbour ($x, 1 + y, z$). The chains defined by molecules (1) are parallel to the *c* axis, those of molecules (2) are parallel to the *b* axis.

There is only one hydroxyl group in 2,4-diazido-2,4-dideoxy-1,6-anhydro-β-D-glucopyranose which could be a donor in a hydrogen bond. A torsion angle of −154° for C(2)—C(3)—O(3)—H(O3) shows that the H atom is pointing away from the molecule. The acceptor is the anhydro O(1) atom of a symmetry-related neighbour. The O(13)—O(11′) distance is 2·859 (4) Å (symmetry operation $\frac{3}{2} - x, 2 - y, \frac{1}{2} + z$), and the O(23)—O(21′) distance is 2·977 (5) Å ($1 - x, \frac{1}{2} + y, \frac{1}{2} - z$). However, the hydrogen distances are very long: H(O13)—O(11) is 2·26 (6) and H(O23)—O(21) is 2·32 (6) Å. The angles at H(O3) are 148 and 152° for molecules (1) and (2) respectively.

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References

Berking, B. & Seeman, N. N. (1971). *Acta Cryst.* B**27**, 1752–1760.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Brown, G. M. & Thiessen, W. E. (1969). *Acta Cryst.* A**25**, S195.

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

Foces-Foces, C., Cano, F. H. & García-Blanco, S. (1976). *Acta Cryst.* B**32**, 427–430.

Hecht, H.-J., Luger, P. & Reinhardt, R. (1977). *J. Cryst. Mol. Struct.* **7**, 161–171.

Jeffrey, G. A., Pople, J. A., Binkley, J. S. & Vishveshwara, S. (1978). *J. Am. Chem. Soc.* **100**, 373–379.

Jeffrey, G. A., Pople, J. A. & Radom, L. (1972). *Carbohydr. Res.* **25**, 117–131.

Jeffrey, G. A., Pople, J. A. & Radom, L. (1974). *Carbohydr. Res.* **38**, 81–95.

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.

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.

Małuszyńska, H., Takagi, S. & Jeffrey, G. A. (1977). *Acta Cryst.* B**33**, 1792–1796.

Noordik, J. H. & Jeffrey, G. A. (1977). *Acta Cryst.* B**33**, 403–408.

Panagiotopoulos, N. C. (1974). *Acta Cryst.* B**30**, 1402–1407.

Park, Y. J., Kim, H. S. & Jeffrey, G. A. (1971). *Acta Cryst.* B**27**, 220–227.

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

Paulsen, H., Györgydeak, Z. & Friedmann, M. (1974*a*). *Chem. Ber.* **107**, 1568–1578.

Paulsen, H., Györgydeak, Z. & Friedmann, M. (1974*b*). *Chem. Ber.* **107**, 1590–1613.

Paulsen, H. & Koebernick, H. (1976). *Chem. Ber.* **109**, 104–111.

Romers, C., Altona, C., Buys, H. R. & Havinga, E. (1969). *Top. Stereochem.* **4**, 73–77.

Salathiel, W. M. & Curl, R. F. Jr (1965). *J. Chem. Phys.* **44**, 1288–1290.

Stewart, J. M., Machin, P. A., Ammon, H. L., Dickinson, C., Heck, H. & Flack, H. (1976). The XRAY 76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Trnka, T., Cerny, M., Budesinsky, M. & Pacek, J. (1975). *Collect. Czech. Chem. Commun.* **40**, 3038–3045.