

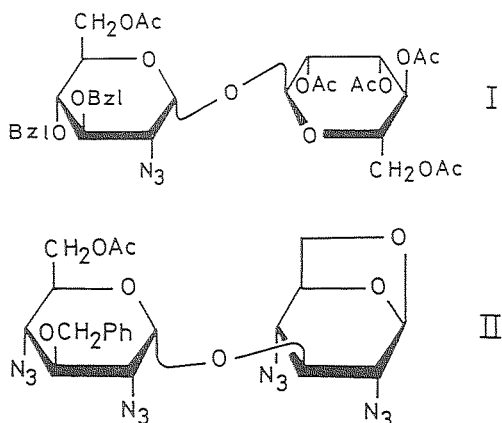
09.2-10 CRYSTAL STRUCTURE OF METHYL 4,6-O-(S)-BENZYLIDENE-2-CHLORO-2-DEOXY- α -D-IDOPYRANOSIDE. By I.A.S. Edwards, H.P. Stadler and L.N. Chamberlain, School of Chemistry, The University, Newcastle upon Tyne, U.K.

The structure was determined from Weissenberg photographs, the crystals belong to space group $P2_1$ with two molecules per unit cell, and $a=11.83$, $b=12.70$, $c=4.62\text{\AA}$, $\beta=91.8^\circ$. Refinement led to an R value of 0.081 using visually estimated intensities correlated by double slit photographs. The structure was determined from sharpened Patterson sections and refined by least squares.

While most previous structure determinations of sugars show the pyranoid ring in the chair conformation, the idopyranoside described has an ideal skew conformation, 0S_2 , half-way between $B_{5,2}$ and $B_{3,0}$. This conformation allows all the non-H substituents to lie in equatorial positions, generally regarded as the most stable. In addition, the dioxane ring has a chair conformation with the phenyl group equatorial.

A 2.88\AA intermolecular H-bond from the pyranose oxygen to the OH on C3 may further stabilize the 0S_2 conformation in the solid.

09.2-11 HIGHLY SUBSTITUTED DISACCHARIDES WITH UNUSUAL α -LINKAGES. By H.-J. Schmidt, M. Strumpel, P. Luger; Institut für Kristallographie, FU Berlin and H. Paulsen, Institut für Organische Chemie und Biochemie, Universität Hamburg; Federal Republic of Germany. We have investigated two highly substituted disaccharides, both having unusual glycosidic linkages. The first, 2,3,4,6-tetra-O-acetyl- α -D-mannopyranosyl-6-O-acetyl-2-azido-3,4-di-O-benzyl-2-deoxy- α -D-glucopyranoside (I) is a manno-trehalose derivative having an $\alpha, \alpha(1\rightarrow1)$ glycosidic linkage. The second, 3-O-(6-O-acetyl-2,4-diazido-3-O-benzyl-2,4-dideoxy- α -D-glucopyranosyl)-1,6-anhydro-2,4-diazido-2,4-dideoxy- β -D-glucopyranose (II), is composed of two diazido glucose residues, of which one is present in the β -1,6-anhydro form and therefore is forced to adopt the 1C_4 -conformation.



Because of this the $\alpha(1\rightarrow3)$ linkage connects a 4C_1 and a 1C_4 pyranosyl chair being investigated for the first time by X-ray methods. The common feature of both disaccharides is that the linkage is axial with respect to both pyranosyl rings and that the conformation around the glycosidic linkages is very similar (see Fig.1). This conformation is equal to that of all gluco-trehalose structures so far investigated. Disaccharides which are (1+1)-linked contain the characteristic C-O-C-O-C-O-C-sequence. Because of the α configuration of both rings and an arrangement of the glycosidic oxygen bonds which is near to (+sc,+sc), the four inner bonds of that sequence are shortened to 1.405\AA (mean value) whereas the outer bonds are 1.436\AA (mean). Both of the chairs of I and the 4C_1 chair of II adopt nearly the perfect chair conformation. Like most 1,6 anhydro pyranoses investigated previously the 1C_4 anhydro-bridged chair shows a conformation half between 1C_4 and E_0 . This conformation is caused mainly by the anti-reflex-effect of the anhydro-bridge and by trans-annular N---O interactions.

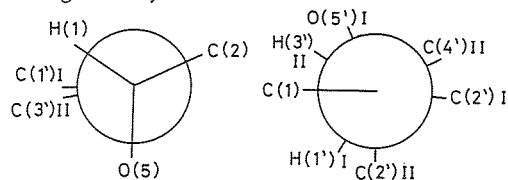


Fig.1: Conformational situation along the glycosidic bonds C(1)-O(1) (left) and O(1)- $\begin{cases} C(1') (I) \\ C(3') (II) \end{cases}$ (right)

09.2-12 CRYSTALLIZATION AND STRUCTURE DETERMINATION OF TETRAHYDROPYRAN. By J. Buschmann and P. Luger, Institut für Kristallographie, Fachbereich Chemie, Freie Universität Berlin, Takustr. 6, D-1000 Berlin 33, Germany.

Engaged in structure investigations of basic compounds in carbohydrate chemistry we have obtained a crystallization product of Tetrahydropyran (THP) at a temperature of about -75°C , which is suited for single crystal x-ray diffraction measurements. The melting point of THP is at -49°C . Substance is sealed in a thin-walled glass capillary; temperature is controlled by the gas stream method with an intermediary heating, using liquid nitrogen as the gas stream source; crystallization is achieved with the aid of an electronically controlled heated coil positioned around the capillary; and measurements are so far done only with film methods.

A crystal of THP has been found to be cubic with a lattice constant of $a = 10.4\text{\AA}$. The number of formula units per unit cell is eight. A possible space group which includes some pseudosymmetry, is $P4_3n$. Intensity data collection and structure determination are in progress. - This work is supported by the German Research Community (Deutsche Forschungsgemeinschaft).