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## The Crystal and Molecular Structure of 1,2-*O*-Aminoisopropylidene- $\alpha$ -D-glucopyranose Hydroiodide

BY JAMES TROTTER\* AND J. K. FAWCETT

*Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada*

(Received 25 June 1965 and in revised form 4 January 1966)

Crystals of 1,2-*O*-aminoisopropylidene- $\alpha$ -D-glucopyranose hydroiodide are monoclinic,  $a = 10.09$ ,  $b = 7.88$ ,  $c = 8.16$  Å,  $\beta = 100.6^\circ$ ,  $Z = 2$ , space group  $P2_1$ . The intensities of 1360 reflexions were measured with a scintillation counter and Mo  $K\alpha$  radiation. The iodide ion position was determined by Patterson methods, and all carbon, nitrogen, and oxygen atoms were located from two three-dimensional electron-density distributions. The positional and anisotropic thermal parameters of the seventeen I, C, N, O, atoms in the asymmetric unit were refined by least-squares, and all the hydrogen atoms (except those of the CH<sub>3</sub> group) were located from an ( $F_o - F_c$ ) synthesis; the final  $R$  value is 0.089.

The previously unknown configuration of the asymmetric dioxolane 2-carbon atom is determined, and the absolute configuration is established since the compound is derived from D-glucose. The five-membered ring has an envelope conformation, with the dioxolane 2-carbon atom displaced 0.36 Å from the plane of the other four atoms, and the pyranose ring has a flattened chair conformation. The dihedral angles are different from those deduced from a previous proton magnetic resonance (p.m.r.) study, but the p.m.r. data can be reinterpreted in terms of a conformation similar to that found in the present analysis. The bond distances and valency angles are normal. The crystal is held together by a system of O-H  $\cdots$  O (2.69 Å), N-H  $\cdots$  O (2.74, 2.85, 3.03 Å), and O-H  $\cdots$  I<sup>-</sup> (3.39, 3.47 Å) hydrogen bonds.

### Introduction

In a study of the proton magnetic resonance (p.m.r.) spectra of a series of 1,2-*O*-alkylidene- $\alpha$ -D-glucopyranoses, Coxon & Hall (1964) suggested that the pyranose ring in these derivatives adopts, not the expected flattened chair, but essentially a skewed boat conformation. This deduction was made by measuring the vicinal proton-coupling constants, and using the Karplus (1959, 1963) equation,

$$J = J_0 \cos^2 \varphi - K$$

\* Alfred P. Sloan Foundation Fellow.

to calculate the dihedral angles<sup>†</sup> ( $\varphi$ ) from the coupling constants ( $J$ ),  $J_0$  and  $K$  being empirically derived constants. Since this equation involves a  $\cos^2 \varphi$  dependence, two angles may be calculated for each coupling constant, and Coxon & Hall chose acute dihedral angles between H(1) and H(2), between H(2) and H(3), and between H(3) and H(4), with values in the range about 40–60° for the various compounds, and angles close to 180° for the H(4), H(5) dihedral angles. These choices were made by comparison with compounds of known chair conformation, in which the dihedral angles are

† The dihedral angle between two hydrogen atoms on adjacent carbon atoms is the angle between the C–H bonds when they are viewed along the axis of the C–C bond.

all either  $180^\circ$ , giving a large coupling constant, or  $60^\circ$ , giving a small coupling constant. Small coupling constants were assumed to be indicative of small dihedral angles. This would appear however to be a very dangerous assumption, since there is no reason to suppose that, in an irregular conformation, an ideal  $180^\circ$  angle might not be reduced to say  $120^\circ$ , and hence give rise to a small coupling constant. In fact if the H(2), H(3) and H(3), H(4) dihedral angles are taken as about  $130^\circ$ , rather than  $50^\circ$  as derived by Coxon & Hall, then the compounds do not have the 'skew boat' conformation, which involves a conformational inversion about the C(2)–C(3) bond of the more usual chair form, but have a distorted chair form, and the alkylidene group would be expected to produce some distortion in an ideal chair conformation.

It seemed that an X-ray crystal structure investigation of a compound of this type would assist in the interpretation of the p.m.r. spectra, although care would be required in making comparison between a measured conformation in the solid, and deduced conformations in solution. In addition, Coxon & Hall (1964) point out that in none of their derivatives which possess an asymmetric dioxolane 2-carbon atom [using the nomenclature of Coxon & Fletcher (1963)] is the absolute configuration of this carbon atom known, and this configuration could certainly be determined by crystal structure analysis. The compound chosen for X-ray study was the hydroiodide of 1,2-*O*-aminoisopropylidene- $\alpha$ -D-glucopyranose, which was prepared from 2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-glucopyranosyl bromide (Coxon & Fletcher, 1963).

### Experimental

Crystals of 1,2-*O*-aminoisopropylidene- $\alpha$ -D-glucopyranose hydroiodide from aqueous isopropanol-ether are needles elongated along *c*. The unit-cell parameters and space group were determined from various rotation and Weissenberg photographs and on the General Electric spectrogoniometer.

*Crystal data* ( $\lambda$ , Cu  $K\alpha$  = 1.5418 Å;  $\lambda$ , Mo  $K\alpha$  = 0.7107 Å) 1,2-*O*-aminoisopropylidene- $\alpha$ -D-glucopyranose hydroiodide, C<sub>9</sub>H<sub>18</sub>O<sub>6</sub>NI; M.W. 363.2; m.p. 151°C.

Monoclinic,  $a = 10.09 \pm 0.01$ ,  $b = 7.88 \pm 0.01$ ,  $c = 8.16 \pm 0.01$  Å,  $\beta = 100.6^\circ \pm 0.1^\circ$ .

$U = 637.3$  Å<sup>3</sup>.

$D_m = 1.88$  (floatation in carbon tetrachloride-bromofrom),  $Z = 2$ ,  $D_x = 1.90$  g.cm<sup>-3</sup>.

Absorption coefficient for X-rays,  $\mu(\text{Mo } K\alpha) = 26$  cm<sup>-1</sup>.  $F(000) = 360$

Absent spectra:  $0k0$  when  $k$  is odd. Space group  $P2_1$  ( $C_2^1$ ) ( $P2_1/m$  being excluded since the compound is optically active).

The intensities of all reflexions with  $2\theta(\text{Mo } K\alpha) \leq 53^\circ$  (corresponding to a minimum interplanar spacing  $d = 0.80$  Å) were measured on a General Electric XRD-5

Spectrogoniometer with Single Crystal Orienter, using a scintillation counter, Mo  $K\alpha$  radiation (zirconium filter and pulse height analyser), and the moving-crystal moving-counter technique (Furnas, 1957). All the intensities were corrected for background (approximately a function of  $\theta$  only) and the structure amplitudes were derived as usual. The crystal was mounted with  $c^*$  parallel to the axis of the goniostat, and had cross-section  $0.3 \times 0.2$  mm. Possible errors in the measured structure factors as a result of absorption were estimated in two ways. Firstly, taking the crystal as a cylinder of mean diameter 0.25 mm,  $\mu R$  is 0.32, and hence the maximum absorption error in the range  $\theta = 0^\circ$ – $26.5^\circ$  is only about  $\frac{1}{2}\%$  in structure factor (*International Tables for X-ray Crystallography*, 1959). Secondly, a possibly more serious source of error, non-uniformity of the crystal dimensions, was considered. A reasonable estimate of the errors may be obtained by considering the longest and shortest path lengths in the crystal cross-section, 0.36 and 0.20 mm respectively. The absorption corrections to the structure factors for these path lengths are  $\exp\{26 \times 0.036/2\}$  and  $\exp\{26 \times 0.02/2\}$ , that is 1.60 and 1.30 respectively, so that the *maximum* deviation from the mean correction is 10%. Since the *maximum* error in  $F_o$  due to absorption is 10%, and since most of the errors will be much less than this value, no corrections for absorption were applied. 1360 reflexions in the range  $0 < 2\theta \leq 53^\circ$  were observed, 95% of the total number of reflexions in this range.

### Structure analysis

The position of the iodide ion was determined from the [010] Patterson projection as (0.170, 0, 0.140), and structure factors were calculated for all the three-dimensional data for the iodine only. The scattering factor for I<sup>-</sup> was obtained from the curve for uncharged iodine (*International Tables for X-ray Crystallography*, 1962) by comparison with the differences in the values of X<sup>-</sup> and X (X = F, Cl, Br); it was corrected for anomalous dispersion, according to the expression

$$f(\text{corrected}) = \sqrt{[(f_1^- + \Delta f_1')^2 + (\Delta f_1'')^2]}$$

using the values  $\Delta f'$ ,  $\Delta f''$  given in *International Tables* (1962). The isotropic thermal parameter,  $B$ , was taken as  $4.5$  Å<sup>2</sup>. The discrepancy index,  $R$ , was 0.39 for the observed reflexions. A three-dimensional Fourier series was summed with phases based on the iodine atom; since  $y_1$  was (arbitrarily) zero, the resulting electron-density distribution had a false mirror plane at  $y = 0$ . Despite this it was possible to pick out all carbon, oxygen, and nitrogen atoms. These were introduced into the structure factor calculations with the scattering factors of *International Tables* (1962) and  $B = 4.5$  Å<sup>2</sup>.  $R$  was reduced to 0.21 and a second three-dimensional electron-density distribution gave sharply resolved peaks for all 17 atoms.

Further refinement of the positional and isotropic thermal parameters, together with an overall scale fac-

tor, proceeded by (block-diagonal) least squares, the function minimized being  $\sum w(|F_o| - |F_c|)^2$ . Since the structure factors were considered to be least accurately measured for the very strong reflexions, which are most affected by extinction, and for weak reflexions, for which the intensities are close to background, the weighting scheme used was  $\sqrt{w} = |F_o|/F^*$  when  $|F_o| < F^*$ , and  $\sqrt{w} = F^*/|F_o|$  when  $|F_o| \geq F^*$ .  $F^*$  was taken as 30. After five cycles of isotropic least-squares refinement  $R$  was 0.14, and all the parameter shifts were small and in random directions, the largest parameter shift in the fifth cycle being one-third of a standard deviation. At this stage the interatomic distances and angles were computed, and all the values seemed normal except the intermolecular distances involving the nitrogen atom. The nitrogen atom made three contacts

with oxygen atoms, O(13), O(14) and O(15) of different molecules (see Fig. 1 for atom numbering, and Fig. 2 for the final packing diagram), and it seemed likely that these corresponded to N-H...O hydrogen bonds. The N...O(14) distance was 2.95 Å, reasonable for an N-H...O hydrogen bond (range of 2.55–3.1 Å given by Fuller (1959), for example, in a review of hydrogen-bonded structures). The N...O(13) and N...O(15) distances measured 2.49 and 3.33 Å respectively; the first of these distances was shorter than any distance reported previously for a bond of this type, the shortest reported value being 2.55 Å in cysteylglycine sodium iodide (Dyer, 1952), and the 3.33 Å distance seemed to be too long to represent a hydrogen bond. This unsymmetrical arrangement about the nitrogen atom suggested that some of the positional parameters might

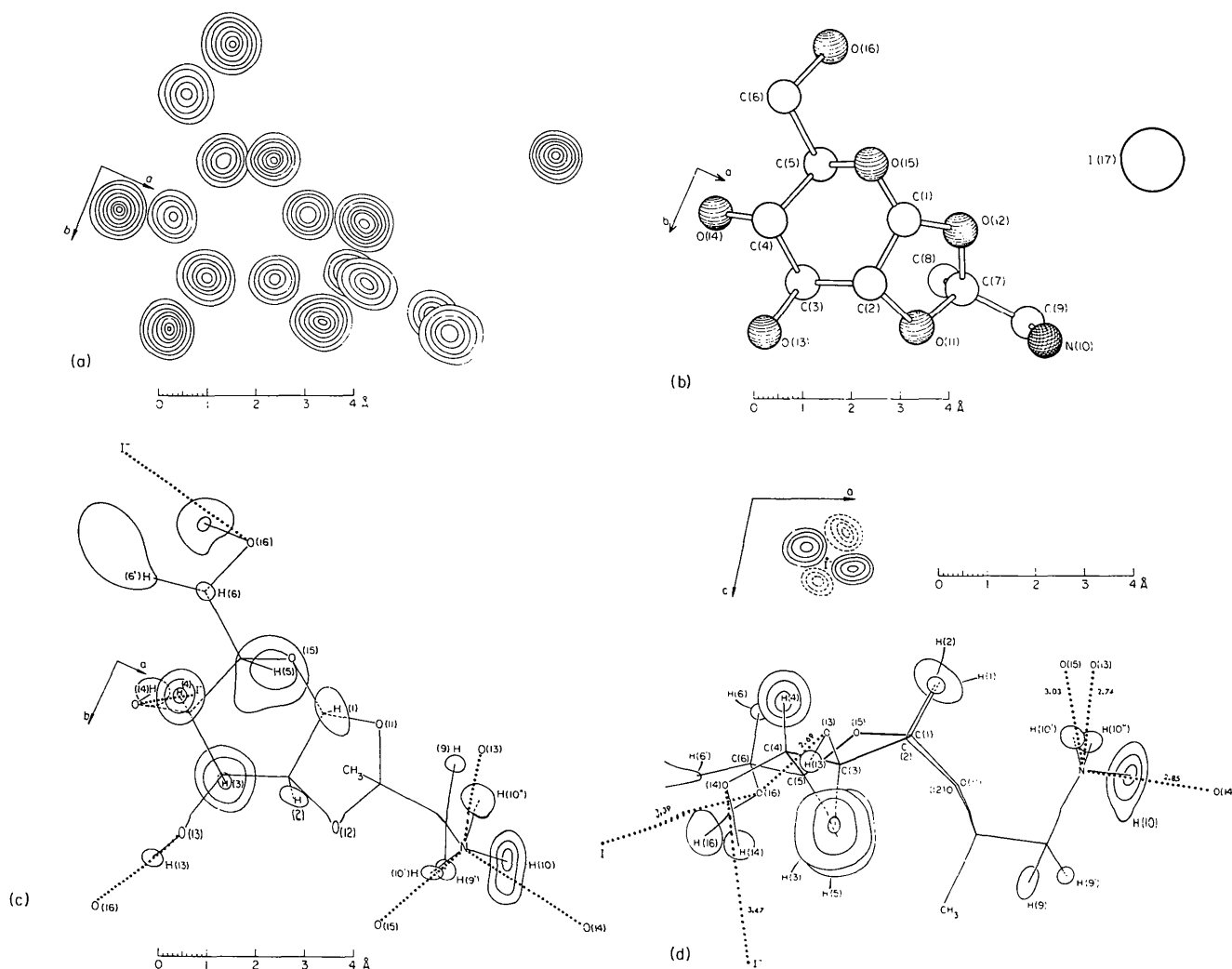
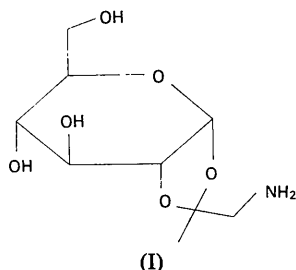


Fig. 1. (a) Superimposed sections of the three-dimensional electron-density distribution, taken through the atomic centres parallel to (001). Contours are at intervals of  $2 \text{ e.}\text{\AA}^{-3}$  for C, N, O atoms, and  $20 \text{ e.}\text{\AA}^{-3}$  for  $\text{I}^-$ . The map is drawn with the positive direction of the  $c^*$  axis away from the viewer, so that the diagram can be compared directly with formula (I), and the correct absolute configuration is shown. (b) Perspective drawing of the molecule showing the atom numbering used. The  $c^*$  axis points away from the viewer as in Fig. 1(a). (c) and (d) Two views of the three-dimensional difference synthesis, showing the hydrogen atoms. Contours at intervals of  $0.5 \text{ e.}\text{\AA}^{-3}$  ( $\pm 1 \text{ e.}\text{\AA}^{-3}$  around  $\text{I}^-$ ). In (c), the  $c^*$  axis points away from the viewer; in (d) the  $b$  axis points towards the viewer.

be in error. An examination of the structure (final positions in Fig. 1 and Table 2) shows that many of the atoms occur in pairs related by a pseudo-mirror plane at  $y=0$ , and that four atoms, C(7), C(8), C(9), and N(10) lie very close to this mirror plane. Atoms C(7) and C(8) had initially been given  $y$  coordinate zero, but C(9) had been given  $y=+0.02$ , and N(10)  $y=-0.02$  in accordance with the second three-dimensional electron-density distribution; the refined  $y$  coordinates differed only slightly from these values. Since however an atom originally displaced in the wrong direction from  $y=0$  would possibly not refine across the pseudo-mirror plane, it seemed judicious to set the  $y$  parameters of C(7), C(8), C(9), and N(10) equal to zero before continuing the refinement. This procedure immediately reduced  $R$  by about 1% to 0.13, and the refinement again converged (maximum shift  $0.3\sigma$ ) after three further isotropic least-squares cycles, giving  $R=0.126$ . C(7), C(8), and C(9) had refined to the same positions as previously, but N(10) refined to  $y=+0.03$ , giving a more symmetrical arrangement of hydrogen bonds.



At this stage three-dimensional  $F_o$  and  $(F_o - F_c)$  syntheses were computed. Sections of the resulting electron-density distribution are shown in Fig. 1(a). All the atoms are very well resolved, the peak densities being  $140 \text{ e.}\text{\AA}^{-3}$  at the iodide ion,  $9\text{--}10 \text{ e.}\text{\AA}^{-3}$  at car-

bon,  $11 \text{ e.}\text{\AA}^{-3}$  at nitrogen, and  $12\text{--}14 \text{ e.}\text{\AA}^{-3}$  at oxygen. These high peaks are a consequence of the relatively low thermal parameters (Table 2), which are probably due to the compact hydrogen-bonding scheme, and not simply to absorption (see *Experimental* above, where variation of absorption with Bragg angle is shown to be negligible.) A drawing of the molecule is shown in Fig. 1(b), and two different views of the most significant features of the three-dimensional difference map are shown in Fig. 1(c) and (d). The most outstanding fluctuations in difference density are peaks and troughs of  $\pm 4 \text{ e.}\text{\AA}^{-3}$  associated with the iodide ion [Fig. 1(d)], clearly indicative of anisotropic thermal motion. In addition there is a negative trough of about  $-2 \text{ e.}\text{\AA}^{-3}$  (omitted from Figs. 1(c) and 1(d) for clarity) running the whole length of the cell in the  $b$  direction directly between the iodide ions, with associated positive regions as high as  $+1.5 \text{ e.}\text{\AA}^{-3}$ . All of this density is fairly obviously associated with required adjustments in the iodide thermal parameters. The next most significant features [Fig. 1(c) and (d)] are four peaks of about  $1.5 \text{ e.}\text{\AA}^{-3}$  close to atoms C(3), C(4), C(5), and N(10); these peaks are in positions where one would expect hydrogen atoms, and they no doubt do correspond to these hydrogen atoms. The density throughout the remainder of the map does not exceed  $\pm 1 \text{ e.}\text{\AA}^{-3}$ , and a small peak of  $\frac{1}{2}\text{--}1 \text{ e.}\text{\AA}^{-3}$  is present close to every expected hydrogen position [Fig. 1(c) and (d)], except for the methyl group hydrogens. There are several small peaks near C(8) none of which could be definitely ascribed to hydrogen. These smaller hydrogen peaks do not of course stand out as well as Figs. 1(c) and 1(d) suggest, since they are of the same height as many other small density fluctuations, which are omitted from the figure for clarity. Positional parameters were determined from the difference map for all the hydrogen atoms except those of the methyl group.

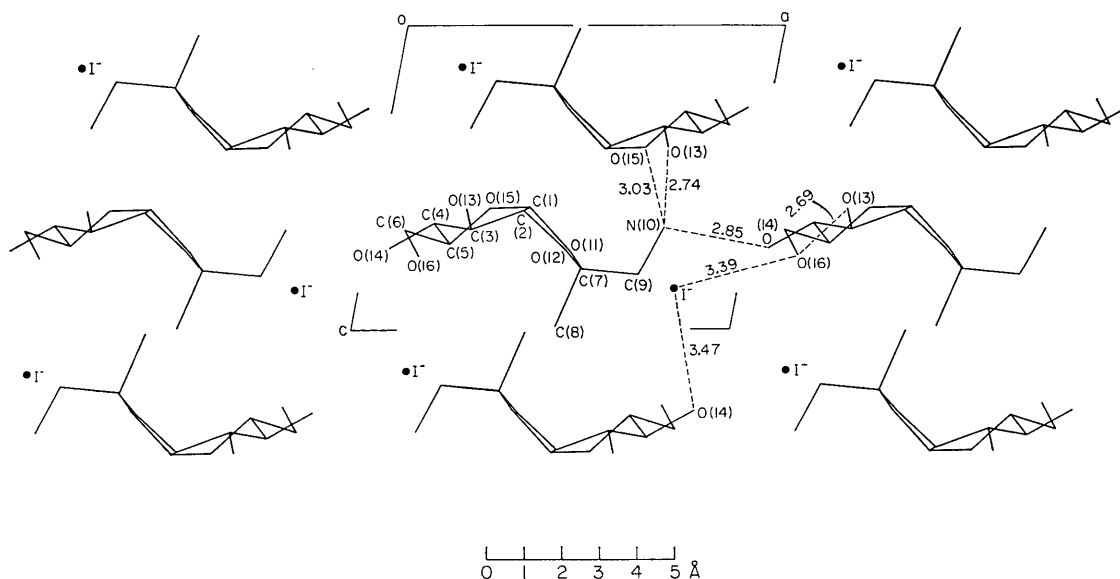


Fig. 2. Projection of the structure along [010], showing the molecular packing. One hydrogen bond of each type is shown.



Table 1 (cont.)

A large grid of numerical data organized into columns and rows, with various labels like H5L, H7L, L=0, L=1, L=2, L=3, L=4, L=5, L=6, L=7, L=8, L=9, L=10, L=11, L=12, L=13, L=14, L=15, L=16, L=17, L=18, L=19, L=20, L=21, L=22, L=23, L=24, L=25, L=26, L=27, L=28, L=29, L=30, L=31, L=32, L=33, L=34, L=35, L=36, L=37, L=38, L=39, L=40, L=41, L=42, L=43, L=44, L=45, L=46, L=47, L=48, L=49, L=50, L=51, L=52, L=53, L=54, L=55, L=56, L=57, L=58, L=59, L=60, L=61, L=62, L=63, L=64, L=65, L=66, L=67, L=68, L=69, L=70, L=71, L=72, L=73, L=74, L=75, L=76, L=77, L=78, L=79, L=80, L=81, L=82, L=83, L=84, L=85, L=86, L=87, L=88, L=89, L=90, L=91, L=92, L=93, L=94, L=95, L=96, L=97, L=98, L=99, L=100. Each cell contains numerical values, often with a leading sign (+/-).

Table 2. Final positional parameters (fractional x 10^4) and standard deviations (Å x 10^3), isotropic thermal parameters, and anisotropic thermal parameters\*

A table with two main sections. The first section lists atoms from C(1) to I(17) with columns for x, y, z, σ(x), σ(y), σ(z), B(Å²), and σ(B). The second section lists atoms from C(1) to I(17) with columns for U11, U12, U13, U22, U23, U33, and Mean σ(U).

\* Uij are the components of the vibration tensors in matrix form in Å² x 10².

Throughout all the refinement stages the scattering factor used for nitrogen was that for the uncharged atom, and this gave a reasonable value for the nitrogen thermal parameter. It seems likely however that the positive charge is on the  $\text{NH}_3^+$  group.

The final measured and calculated structure factors and the calculated phase angles are listed in Table 1;  $R$  is 0.089 for the 1360 observed reflexions. A final three-dimensional difference synthesis was computed; this map still showed peaks and troughs as high as  $\pm 2 \text{ e.}\text{\AA}^{-3}$  associated with the iodide ion, but since these may very well be a result of absorption errors in the data, no further effort was made to remove them. The density in the rest of the map was all between  $\pm 1 \text{ e.}\text{\AA}^{-3}$ .

The positional and anisotropic thermal parameters of the heavier atoms, from the final least-squares cycle, are given in Table 2, together with their standard deviations computed from the inverses of the diagonal terms of the matrix of the least-squares normal equations. The isotropic thermal parameters, from the last isotropic cycle, are also given in Table 2. Table 3 gives the hydrogen positional parameters from the three-dimensional difference synthesis;  $B$  was taken as  $3.0 \text{ \AA}^2$  for all the hydrogen atoms, and none of the hydrogen parameters was refined in the least-squares cycles. The atom numbering used is shown in Fig. 1.

Table 3. *Hydrogen positional parameters (fractional  $\times 10^3$ ;  $B$  taken as  $3.0 \text{ \AA}^2$  for all hydrogen atoms)*

Atom	$x$	$y$	$z$
H(1)	440	-100	460
H(2)	437	130	467
H(3)	300	170	807
H(4)	143	018	500
H(5)	290	-145	827
H(6)	100	-260	540
H(6')	0	-225	700
H(9)	700	-125	933
H(9')	763	110	907
H(10)	867	025	690
H(10')	733	135	587
H(10'')	773	-070	607
H(13)	213	405	653
H(14)	087	040	847
H(16)	037	-420	833

## Discussion

### *Molecular structure and dimensions*

The analysis has established the structure, including the previously unknown configuration of the dioxolane 2-carbon atom (C(7) in the numbering used for convenience in the crystal analysis), of 1,2-*O*-aminoisopropylidene- $\alpha$ -D-glucopyranose hydroiodide, as that shown in the perspective drawing in Fig. 1(b). It is clear from Fig. 1(d) and Fig. 2 that the five-membered ring is slightly non-planar, having an envelope conformation (described in more detail below), and that the aminomethyl group is in the equatorial position (the ring is actually not very far from being planar, but the aminomethyl group may be described at least as pseudo-

equatorial). It may be noted in addition that, since the compound is derived from D-glucose, the *absolute* configuration is established; the positional parameters of Table 2, referred to a conventional right-handed set of axes, give the correct absolute configuration, which is also depicted in all the diagrams. The hydrogen atom positions have also been determined, but with less precision than for the heavier atoms. From a comparison of the curvatures of the hydrogen atoms in the ( $F_o - F_c$ ) synthesis and those of the heavier atoms in the  $F_o$  synthesis, it is estimated that the standard deviations of the hydrogen atom positional parameters are about ten times those of the carbon atoms, that is about  $0.2 \text{ \AA}$ .

The bond distances and valency angles in the molecule are given in Table 4. The mean C-C distance is  $1.50 \text{ \AA}$ , and the mean C-O distance is  $1.44 \text{ \AA}$ , the estimated standard deviations of the individual distances being in the range  $0.023\text{--}0.028 \text{ \AA}$ . These bond lengths are similar to those in other pyranoid sugars, where the mean C-C distances are  $1.51\text{--}1.53 \text{ \AA}$ , and the mean C-O distances  $1.41\text{--}1.44 \text{ \AA}$  (Jeffrey & Rosenstein, 1964). There are some deviations from the mean values as large as  $2\sigma$ , and one deviation of nearly  $3\sigma$  [for

Table 4. *Bond distances and valency angles\**

C(1)-C(2)	1.47 $\text{\AA}$	C(1)-O(11)	1.44 $\text{\AA}$
C(2)-C(3)	1.55	C(1)-O(15)	1.36
C(3)-C(4)	1.44	C(2)-O(12)	1.46
C(4)-C(5)	1.57	C(3)-O(13)	1.46
C(5)-C(6)	1.46	C(4)-O(14)	1.47
C(7)-C(8)	1.52	C(5)-O(15)	1.45
C(7)-C(9)	1.49	C(6)-O(16)	1.44
Mean C-C	1.50	C(7)-O(11)	1.47
		C(7)-O(12)	1.41
C(9)-N(10)	1.45	Mean C-O	1.44
C(2)-C(1)-O(11)	103°	C(5)-C(6)-O(16)	113°
C(2)-C(1)-O(15)	120	C(8)-C(7)-C(9)	111
O(11)-C(1)-O(15)	114	C(8)-C(7)-O(11)	108
C(1)-C(2)-C(3)	116	C(8)-C(7)-O(12)	119
C(1)-C(2)-O(12)	108	C(9)-C(7)-O(11)	109
C(3)-C(2)-O(12)	109	C(9)-C(7)-O(12)	106
C(2)-C(3)-C(4)	112	O(11)-C(7)-O(12)	104
C(2)-C(3)-O(13)	108	C(7)-C(9)-N(10)	115
C(4)-C(3)-O(13)	112	Mean at C	110
C(3)-C(4)-C(5)	111		
C(3)-C(4)-O(14)	110	C(1)-O(11)-C(7)	112
C(5)-C(4)-O(14)	108	C(2)-O(12)-C(7)	108
C(4)-C(5)-C(6)	112	C(1)-O(15)-C(5)	118
C(4)-C(5)-O(15)	103	Mean C-O-C	113
C(6)-C(5)-O(15)	109		
C(1)-H(1)	1.1 $\text{\AA}$	N(10)-H(10)	0.9 $\text{\AA}$
C(2)-H(2)	1.3	N(10)-H(10')	1.1
C(3)-H(3)	1.1	N(10)-H(10'')	1.0
C(4)-H(4)	1.1		
C(5)-H(5)	1.2	O(13)-H(13)	1.0
C(6)-H(6)	1.1	O(14)-H(14)	1.1
C(6)-H(6')	1.1	O(16)-H(16)	1.3
C(9)-H(9)	1.4		
C(9)-H(9')	1.0		

Angles involving hydrogen =  $86^\circ\text{--}123^\circ$  (except for H(9), where two angles are  $73^\circ$  and  $135^\circ$ ).

\* The standard deviations are: Bonds and angles not involving hydrogen,  $0.023\text{--}0.028 \text{ \AA}$ ,  $1.1^\circ\text{--}1.8^\circ$ ; Bonds and angles involving hydrogen,  $0.2 \text{ \AA}$  and  $10^\circ$ .

C(1)–O(15)], but these variations cannot be considered as really significant. The angles in the six-membered ring are in the range 103°–120°, the mean angle within the ring at the carbon atoms being 112°, and the angle at O(15) is 118°. The oxygen angle lies within the range of 112°–120° found in other sugars, and the angles at carbon lie within the range 102°–115° found in other sugars (Jeffrey & Rosenstein, 1964), except for the angles at C(1) and C(2), which are 116° and 120° respectively. These latter angles are of course those which would be changed most from normal values by the addition of the isopropylidene group to the 1,2-positions. The angles in the five-membered ring are in the range 102°–112°, mean value 107°.

The hydrogen atoms have not, of course, been located with any great accuracy, but none of the C–H, N–H, or O–H bond distances differs significantly from 1.1 Å.

#### Molecular conformation and dihedral angles

Various mean planes were calculated to determine the conformations of the five- and six-membered rings. The five-membered ring is best described in terms of the plane through the system C(1)–C(2)–O(11)–O(12), which has equation:

$$-0.6679X' - 0.0331Y + 0.7436Z' = 1.4375,$$

where  $X'$ ,  $Y$ ,  $Z'$  are coordinates in Å referred to orthogonal axes  $a$ ,  $b$ , and  $c^*$ . The deviations of the atoms from this plane are C(1),  $-0.09$  Å; C(2),  $+0.04$  Å; O(11),  $+0.06$  Å; O(12),  $-0.02$  Å; and C(7),  $+0.36$  Å. The system C(1)–C(2)–O(11)–O(12) is therefore approximately planar, with C(7) displaced by 0.36 Å, so that the ring conformation may be described as an envelope.

It is possible to describe the conformation of the six-membered ring also in terms of various planes, but a much more instructive description, and one which is more familiar to carbohydrate chemists, is in terms of dihedral angles. The dihedral angles are given in Table 5; the estimated standard deviations are 1.0°–

1.4° for the angles involving carbon and oxygen, and about 14° for hydrogen dihedral angles, so that the limits of error, taken as  $2.3\sigma$ , are about 3° and 30°.

The significance of the measured dihedral angles of Table 5 in describing the conformation of the pyranose ring can best be seen by comparing the angles with the dihedral angles of an ideal chair form, which are all either 60° or 180° (Table 5). Considering first the dihedral angles of the carbon and oxygen atoms, which are more accurately measured than the hydrogen angles, the measured angles around the C(1)–C(2) bond show the largest deviation (about 45°) from the values in a normal chair ring, and the deviation becomes progressively less in going further from the point of attachment of the isopropylidene group: C(2)–C(3), about 30°, C(3)–C(4), about 10°, and C(4)–C(5), about 5°. The conformation of the pyranose ring may therefore be described as a flattened chair, the deviation from a normal chair being greatest at the 1,2-positions, where the five-membered ring is attached, and becoming progressively less around the ring.

Similar conclusions may be drawn from the hydrogen dihedral angles. Although these have been measured much less accurately than the carbon and oxygen angles, the differences from the ideal values are still significant for the H(1), H(2) dihedral angle (about 60° from the ideal chair angle) and for the H(2), H(3) angle (about 40° from the ideal value). These differences are of the same order of magnitude as for the carbon and oxygen angles. The variations of the H(3), H(4) and H(4), H(5) angles from 180° are not large enough to be considered significant.

A comparison may now be made with the ring conformation deduced by Coxon & Hall (1964) from their p.m.r. study. It is immediately apparent that a reinterpretation of the p.m.r. data, in which the H(2), H(3) and H(3), H(4) dihedral angles are taken as greater than 90°, suggests a conformation quite similar to that deduced from the present X-ray study. The reinterpreted p.m.r. dihedral angle values are included in Table 5, the H(4), H(5) angle, which was not obtainable for this compound, being that for related compounds studied by Coxon & Hall. Now of course it may be objected that it is unwise to make comparisons between the conformations of the pyranose ring of a sugar in solution, and in crystals of a hydroiodide derivative, and it is certainly true that there might be differences, due to solvent effects in solution and to intermolecular packing forces, particularly hydrogen-bonding, in the crystalline derivative. However, it seems very unlikely that the compound would have the unusual skewed-boat conformation in solution, and the much more reasonable flattened chair form in the crystalline hydroiodide derivative. This would require that the distorted chair form, which would be the most likely first conformation in the preparation from the glucopyranosyl bromide, undergoes a conformational inversion about the C(2)–C(3) bond to an unusual conformation, which would probably be less stable (since it has bulky sub-

Table 5. Dihedral angles

Bond involved	Atoms*	Dihedral angles		p.m.r.†
		Measured Angle	Ideal chair	
C(1)–C(2)	H(1), H(2)	$3^\circ \pm 30^\circ$	60°	42°
	C(3), O(5)	16 3	60	
	O(1), O(2)	12 3	60	
C(2)–C(3)	H(2), H(3)	142 30	180	134
	O(2), O(3)	90 3	60	
	C(1), C(4)	24 3	60	
C(3)–C(4)	H(3), H(4)	177 30	180	134
	O(3), O(4)	69 3	60	
	C(2), C(5)	50 3	60	
C(4)–C(5)	H(4), H(5)	151 30	180	157
	O(4), C(6)	55 3	60	
	C(3), O(5)	66 3	60	

\* Chemical numbering; for the oxygen atoms the numbers used in Table 2, Fig. 1 *etc.* are the chemical numbers plus ten.

† Reinterpretation of the p.m.r. data of Coxon & Hall (1964); see text.



stituents in axial positions), and that crystallization as a hydroiodide derivative then reinverts the conformation to the flattened chair form.

A much more plausible interpretation is that the compound has the flattened chair conformation both in solution and in the crystalline hydroiodide. The reinterpreted p.m.r. dihedral angles are quite similar to the measured angles of the present X-ray study (Table 5), and any differences may be a result of experimental errors [no limits of error are quoted by Coxon & Hall (1964)], or of actual *small* differences between the conformations in solution and in the crystal.

In conclusion on this point, it may be added that Coxon & Hall (1964) expressed some surprise on deducing an unusual skewed boat conformation, and suggested that the Karplus equation might not apply for these compounds. Later investigators have applied their methods with no such reservations. The results of the present study suggest that conformational information for pyranose rings, deduced from p.m.r. spectra, should be treated with considerable caution.

#### Intermolecular hydrogen bonding

All the intermolecular distances less than 4.5 Å were calculated. The most significant short distances correspond to a beautiful system of O-H...O, N-H...O, and O-H...I<sup>-</sup> hydrogen bonds, in which every active hydrogen takes part. The distances and angles involved are given in Table 6, and the intermolecular packing is illustrated in Fig. 2.

The NH<sub>3</sub><sup>+</sup> group forms three N-H...O hydrogen bonds with oxygen atoms of three separate molecules, with N...O distances of 2.74 Å to O(13), 2.85 Å to O(14), 3.03 Å to O(15), and with angles varying by up

to about 20° from tetrahedral values. These distances and the general arrangement of the bonds around the NH<sub>3</sub><sup>+</sup> group are similar to those in related compounds; Fuller (1959) lists distances in the range 2.55–3.1 Å.

The O(13) hydrogen atom is utilized in an O-H...O bond of 2.69 Å to O(16) of the molecule related by translation *b*, the C-O...O angle being 122°. Again the distance and angle are similar to those in other bonds of this type (Fuller, 1959). The O(14) and O(16) hydrogen atoms form O-H...I<sup>-</sup> bonds of 3.47 Å and 3.39 Å, with C-O...I<sup>-</sup> angles of 107° and 94°. There are few bonds of this type available for comparison, but the distances are close to the 3.4 Å of the N-H...I<sup>-</sup> bond in cleavamine methiodide, for example (Cameraman & Trotter, 1964). One example of each type of hydrogen bond is illustrated in Fig. 2, and the bonds are indicated also in Fig. 1(c) and (d).

In all of the hydrogen bonds the hydrogen atoms are slightly displaced from the line between the hydrogen-bonded atoms, but the accuracy of the hydrogen atom positions is not sufficiently high to determine whether these displacements are significant. The distances and angles involving hydrogen are included in Table 6.

All the other intermolecular distances correspond to van der Waals interactions, with perhaps some ionic attraction between NH<sub>3</sub><sup>+</sup> groups and the I<sup>-</sup> ions; the NH<sub>3</sub><sup>+</sup> and I<sup>-</sup> are separated by about  $\frac{1}{2}b$ , the distances being N...I = 3.98 Å and 4.43 Å, so that any interaction between them is not strong.

The authors are indebted to Dr L.D. Hall for suggesting the problem and for many helpful discussions, and to Dr B. Coxon for the crystal sample. Grateful

Table 6. Intermolecular hydrogen-bond distances and angles

X-H...Y	X...Y	X-H	H...Y	
N(10)-H...O(13) <sup>I</sup>	2.74 Å	1.0 Å	1.8 Å	
N(10)-H...O(14) <sup>III</sup>	2.85	0.9	2.0	
N(10)-H...O(15) <sup>II</sup>	3.03	1.1	1.9	
O(13)-H...O(16) <sup>IV</sup>	2.69	1.0	1.7	
O(14)-H...I <sup>-V</sup>	3.47	1.1	2.4	
O(16)-H...I <sup>-VI</sup>	3.39	1.3	2.2	
C(9)—N(10)-H(10'')	117°	C(9)-N(10)...O(13) <sup>I</sup>		131°
C(9)—N(10)-H(10)	112	C(9)-N(10)...O(14) <sup>III</sup>		112
C(9)—N(10)-H(10')	119	C(9)-N(10)...O(15) <sup>II</sup>		128
H(10'')-N(10)-H(10)	87	O(13) <sup>I</sup> ...N(10)...O(14) <sup>III</sup>		97
H(10'')-N(10)-H(10')	105	O(13) <sup>I</sup> ...N(10)...O(15) <sup>II</sup>		84
H(10)-N(10)-H(10')	112	O(14) <sup>III</sup> ...N(10)...O(15) <sup>II</sup>		97
C(3)-O(13)-H(13)	120	C(3)-O(13)...O(16) <sup>IV</sup>		122
C(4)-O(14)-H(14)	105	C(4)-O(14)...I <sup>-V</sup>		107
C(6)-O(16)-H(16)	89	C(6)-O(16)...I <sup>-VI</sup>		94
Standard molecule at	<i>x</i>	<i>y</i>	<i>z</i>	
Molecule I at	1 - <i>x</i>	$-\frac{1}{2} + y$	1 - <i>z</i>	
II at	1 - <i>x</i>	$\frac{1}{2} + y$	1 - <i>z</i>	
III at	1 + <i>x</i>	<i>y</i>	<i>z</i>	
IV at	<i>x</i>	1 + <i>y</i>	<i>z</i>	
V at	1 - <i>x</i>	$\frac{1}{2} + y$	2 - <i>z</i>	
VI at	-1 + <i>x</i>	<i>y</i>	<i>z</i>	

acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research under Grant No. PRF 1704-A5. The computations were carried out on the IBM 7040 computer with our own programs, and we thank the staff of the University of British Columbia Computing Centre for assistance.

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### X-Ray Crystallography of the Phenyltriphosphonitriles.

## II. The Crystal Structure of 2,2-Dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene

BY N. V. MANI\*, F. R. AHMED AND W. H. BARNES

*Pure Physics Division, National Research Council, Ottawa 7, Canada*

(Received 31 January 1966)

The crystal structure of 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene,  $\text{Cl}_2(\text{C}_6\text{H}_5)_4\text{P}_3\text{N}_3$ , has been determined by three-dimensional Patterson, Fourier, and difference syntheses. It has been refined to an  $R$  index of 0.091 by differential-synthesis and least-squares methods. The crystals are monoclinic, with  $a = 25.117$ ,  $b = 23.610$ ,  $c = 18.931$  Å,  $\beta = 117^\circ 50'$ ,  $Z = 16$ , space group  $C2/c$ . In the asymmetric unit there are two molecules which are related by translations of almost  $\frac{1}{2}$ ,  $\frac{1}{2}$ , 0 along the directions of the three principal axes. The cyclotriphosphazene ring,  $\text{P}_3\text{N}_3$ , has a slight boat form in contrast to the slight chair form in the diphenyltetrachloro compound. As in the latter there are three sets of P-N bonds of different lengths, 1.556, 1.578, 1.609 Å averaged over the two molecules in the asymmetric unit in the present case. Taking the means for these two molecules, the exocyclic Cl-P-Cl angle is  $98.5^\circ$ , the C-P-C angle is  $104.4^\circ$ , the two types of N-P-N angle are  $120.7^\circ$  and  $115.5^\circ$ , and the two types of P-N-P angle are  $121.0^\circ$  and  $124.9^\circ$ . A few average bond lengths are 1.792 Å for P-C, 2.017 Å for P-Cl, and only 1.376 Å for C-C. The last is virtually identical with the average length of the C-C bond in diphenyltetrachlorocyclotriphosphazene.

#### Introduction

The crystal structure of 2,2-diphenyl-4,4,6,6-tetrachlorocyclotriphosphazatriene,  $(\text{C}_6\text{H}_5)_2\text{Cl}_4\text{P}_3\text{N}_3$ , was recently determined in this laboratory (Mani, Ahmed & Barnes, 1965). The present paper is concerned with the structure of 2,2-dichloro-4,4,6,6-tetraphenylcyclotriphosphazatriene,  $\text{Cl}_2(\text{C}_6\text{H}_5)_4\text{P}_3\text{N}_3$ , the schematic formula of which is shown in Fig. 1 of Mani, Ahmed & Barnes (1965). Whereas crystals of diphenyltetrachlorocyclotriphosphazene showed no extraneous diffraction effects, those of the dichlorotetraphenyl compound presented some difficulties arising from a propensity for reflection twinning across (001), disorder (shown by streaked rows parallel to  $c^*$  and confined almost exclusively to the odd-numbered  $a^*c^*$  and  $b^*c^*$  nets) which appears to be dependent upon the temperature at which the crystals are grown from light petroleum,

and (in one case) the appearance of satellite spots on the streaked rows which vitiates the mirror symmetry across  $c^*$  in the odd-numbered  $b^*c^*$  nets and the diad axis in the corresponding  $a^*c^*$  nets. Of nine crystals examined, the one selected for the structure investigation showed no evidence of twinning, no satellite spots, and only relatively light streaking of reciprocal lattice rows parallel to  $c^*$  on precession photographs even after exposure times of 100 to 200 hours with copper radiation (Ni filter). For all practical purposes, therefore, the selected crystal was virtually ordered. A description and discussion of the interesting diffraction effects observed with the other crystals may be given later in a separate communication.

#### Crystal data

The crystal employed for the determination of the unit-cell constants and for the collection of intensity data was grown from a light-petroleum solution at  $0^\circ\text{C}$ . It

\* National Research Council Postdoctorate Fellow.