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# A Neutron Diffraction Refinement of the Crystal Structures of β-L-Arabinose and Methyl β-D-Xylopyranoside*

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The crystal structures of β-L-arabinose, $C_5H_{10}O_5$, and methyl β-D-xylopyranoside, $C_6H_{12}O_5$, have been refined using neutron diffraction data. In the β-arabinose structure, the hydrogen bonding consists of infinite chains of strong bonds, with H···O distances of 1·735 and 1·801 Å, attached to which are very weak bonds for which H···O is 2·201 Å. There is also a single link from the anomeric hydroxyl to a ring oxygen with H···O 1·820 Å. The hydrogen bonding in the methyl β-xylopyranoside structure is a single finite chain with H···O distances of 1·785 and 1·885 Å, terminating in a weak bond to a ring oxygen (2·088 Å).

## Introduction

The crystal structures of β-L-arabinose (I) and methyl β-D-xylopyranoside (II) were determined by Hordvik (1961) and by Brown, Cox & Llewellyn (1966), respectively, using X-ray diffraction film methods. The main purpose of this refinement was to obtain a more precise description of the hydrogen bonding in these structures.
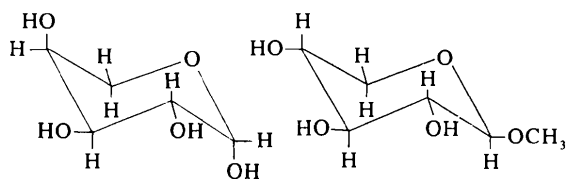


(I)                    (II)

Four pyranose monosaccharide crystal structures have been examined by neutron diffraction: α-D-glucose (Brown & Levy, 1965), methyl α-D-altropyranoside (Poppleton, Jeffrey & Williams, 1975), and methyl α-D-glucopyranoside and methyl α-D-mannopyranoside (Jeffrey, McMullan & Takagi, 1977). Definite rules governing hydrogen-bond geometry are not generally observed (*cf.* Hopfinger, 1973); however, a comparison

of the hydrogen-bond H···O distances in these four carbohydrate structures revealed two interesting correlations. One was a connection between the hydrogen-bond H···O lengths and the type of hydroxyl-to-oxygen interaction. The other was the observation that the anomeric hydroxyl in α-D-glucose is a stronger hydrogen-bond donor and weaker hydrogen-bond acceptor than the other hydroxyl groups (Jeffrey, Gress & Takagi, 1977). There are theoretical reasons why this might be so, as shown by Tse & Newton (1977), and good supporting evidence from X-ray studies (Jeffrey & Lewis, 1977). Nevertheless, further experimental evidence relating to both these observations is necessary and this work is part of a program to obtain this information.

## Experimental

Transparent crystals, with well developed faces, of both compounds were obtained by slow evaporation of 95% ethanol–water solutions at room temperature. The crystal and experimental data and the structure-refinement parameters are given in Table 1. The unit-cell dimensions were determined by least-squares refinement of the setting angles of 29 reflections, which were centered automatically on the neutron diffractometer using the *NEXDAS* program of McMullan (1976).

Table 1. *Crystal data and neutron diffraction experimental and refinement parameters for the crystal structures of β-L-arabinose and methyl β-D-xylopyranoside*

X-ray values are given in square brackets.

| | β-L-Arabinose ($C_5H_{10}O_5$) | Methyl β-D-xylopyranoside ($C_6H_{12}O_5$) |
|---|---|---|
| **Crystal data** | | |
| $a$ | 6·514 (2) Å   [6·513 (1) Å] | 7·877 (2) Å [7·878 (1) Å] |
| $b$ | 19·453 (4)   [19·454 (4)] | 6·933 (3)   [6·938 (1)] |
| $c$ | 4·836 (1)   [4·837 (1)] | 7·748 (2)   [7·747 (1)] |
| $\beta$ | | 113·38 (7)° [113·36 (1)°] |
| $V$ | 612·80 Å³ | 388·39 Å³ |
| $D_m$ | 1·625 g cm⁻³ | 1·406 g cm⁻³ |
| $D_n$ | 1·627 | 1·403 |
| Space group | Orthorhombic, $P2_12_12_1$ | Monoclinic, $P2_1$ |
| $Z$ | 4 | 2 |
| | | |
| **Experimental and refinement data** | | |
| Crystal weight | 0·01272 g | 0·00665 g |
| Crystal volume | 7·827 mm³ | 4·742 mm³ |
| Number of faces | 12 | 13 |
| Crystal habit | {120} {110} {021} {010} {012} | {100} {001} {110} {101} {011} |
| Number of reflections | | |
| Total measured | 2256 ($2\theta_{max} = 112°$), $hkl$ and $h\bar{k}l$ octants | 2442 ($2\theta_{max} = 108°$), $hkl$, $h\bar{k}l$, $hk\bar{l}$, and $h\bar{k}\bar{l}$ octants |
| Averaged | 1004 (7 with $F_o^2 < 0$) | 1059 (8 with $F_o^2 < 0$) |
| Data-collection mode scan width | $\theta$–$2\theta$ step scan with fixed width of 2·4° for $2\theta < 60°$; variable width calculated by 1·0° + 2·75° tan $\theta$ for $2\theta = 60$–112° | $\theta$–$2\theta$ step scan with fixed width of 3° for $2\theta < 60°$; variable width calculated by −0·75° + 5·205° × tan $\theta$ for $2\theta = 60$–108° |
| Wavelength (neutron) | 1·2067 Å | 1·2060 Å |
| Absorption correction | ABSOR (Templeton & Templeton, 1973) | ABSOR (Templeton & Templeton, 1973) |
| $\mu$(neutron) | 2·611 cm⁻¹ | 2·471 cm⁻¹ |
| Maximum correction to $F_o^2$ | 1·650 | 1·486 |
| Minimum correction to $F_o^2$ | 1·408 | 1·389 |
| Average correction to $F_o^2$ | 1·491 | 1·426 |
| | | |
| **Final refinement cycles** | | |
| Number of reflections in refinement, $m$ | 1004 | 1059 |
| Number of variables, $n$ | 182 | 208 |
| $R = \Sigma_H |F_o^2 - k^2 F_c^2|/\Sigma|F_o^2|$ (all reflections) | 0·035 | 0·045 |
| $R_w = (\Sigma_H w|F_o^2 - k^2 F_c^2|^2/\Sigma w|F_o^2|^2)^{1/2}$ (all reflections) | 0·037 | 0·065 |
| $S = [\Sigma_H w|F_o^2 - k^2 F_c^2|^2/(m - n)]^{1/2}$ | 3·75 | 1·21 |
| $w^{-1}$ | $\sigma_c^2(F_o^2) + (0·009\ F_o^2)^2$, where $\sigma_c$ is from counting statistics | $\sigma_c^2(F_o^2) + (0·045\ F_o^2)^2$, where $\sigma_c$ is from counting statistics |
| Extinction parameter, $g$ | 0·62 (4) × 10⁴ | 1·5 (1) × 10⁴ |

The values obtained were in excellent agreement with the X-ray values (given in square brackets in Table 1) which were measured from 25 high $2\theta$ reflections with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1·54051$ Å) on a CAD-4 X-ray diffractometer. The wavelength of the monochromated neutron beam was determined by least squares from the setting angles for 29 reflections of a standard KBr crystal ($a = 6·5966$ Å).

The three-dimensional neutron diffraction data for both crystals were collected at room temperature on a Brookhaven High Flux Beam Reactor single-crystal diffractometer operating under the control of *NEXDAS* (McMullan, 1976). The data-collection procedure is summarized in Table 1. The background was evaluated from counts summed at the scan extremes, using 20% of the total number of points sampled. In the case of the β-L-arabinose crystal, a correction was included for the

scattering of the silica glass fiber on which the crystal was mounted. The data were corrected for absorption using a linear absorption coefficient for neutrons, calculated from the mass absorption coefficient of 23·9 cm$^2$ g$^{-1}$ for hydrogen, which corresponds to a value of 43 barns for the incoherent scattering cross-section.

The atomic coordinates from the X-ray determinations were used as the initial values for refinement by full-matrix least squares, minimizing $\Sigma w|F_o^2 - k^2 F_c^2|^2$ with *FLINUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962). For the β-L-arabinose structure, it was necessary to add 0·25 to the *x*

Table 2. *Fractional coordinates* ($\times 10^5$) *for* β-L-*arabinose and methyl* β-D-*xylopyranoside*

| β-L-Arabinose | x | y | z | β-D-Xylopyranoside | x | y | z |
|---|---|---|---|---|---|---|---|
| C(1) | 74386 (24) | 41714 (7) | 19021 (32) | C(1) | −34717 (15) | 34266 (30) | 23686 (17) |
| C(2) | 68154 (23) | 34626 (7) | 29619 (30) | C(2) | −28622 (14) | 34303 (30) | 7267 (16) |
| C(3) | 49853 (25) | 31985 (7) | 13306 (33) | C(3) | −10136 (15) | 44664 (29) | 13476 (17) |
| C(4) | 32250 (25) | 37179 (8) | 14786 (37) | C(4) | −10762 (16) | 64393 (31) | 21801 (16) |
| C(5) | 40011 (27) | 44153 (9) | 5374 (42) | C(5) | −19092 (27) | 63092 (34) | 36397 (19) |
| O(1) | 81483 (31) | 41002 (9) | −8116 (40) | C(6) | −57286 (29) | 22007 (44) | 33268 (28) |
| O(2) | 85460 (34) | 30199 (9) | 27115 (41) | O(1) | −51909 (20) | 25706 (36) | 18037 (22) |
| O(3) | 43902 (38) | 25464 (10) | 23669 (43) | O(2) | −26511 (23) | 15282 (34) | 1774 (27) |
| O(4) | 24624 (38) | 37734 (13) | 42224 (50) | O(3) | −5410 (22) | 46521 (36) | −2344 (24) |
| O(5) | 57532 (27) | 46298 (8) | 21049 (45) | O(4) | 7373 (23) | 71977 (36) | 30588 (22) |
| HC(1) | 86347 (55) | 43920 (17) | 32467 (80) | O(5) | −36552 (21) | 53700 | 28751 (22) |
| HC(2) | 63934 (54) | 35189 (17) | 51496 (65) | HC(1) | −24551 (39) | 26882 (55) | 35876 (40) |
| HC(3) | 54378 (58) | 31404 (16) | −8515 (64) | HC(2) | −39096 (36) | 42187 (56) | −4518 (38) |
| HC(4) | 20071 (60) | 35596 (23) | 644 (93) | HC(3) | 327 (34) | 35874 (53) | 24353 (44) |
| HC(51) | 28313 (62) | 48097 (19) | 8321 (98) | HC(4) | −19422 (39) | 73932 (50) | 10375 (40) |
| HC(52) | 43973 (68) | 43909 (18) | −16706 (84) | HC(51) | −9586 (47) | 55344 (72) | 48917 (39) |
| HO(1) | 86758 (57) | 45297 (17) | −14326 (79) | HC(52) | −21299 (66) | 77376 (69) | 40757 (67) |
| HO(2) | 86576 (62) | 27370 (18) | 43787 (80) | HC(61) | −60605 (128) | 34991 (127) | 38236 (124) |
| HO(3) | 40421 (62) | 22625 (18) | 7717 (83) | HC(62) | −69229 (78) | 13556 (115) | 28302 (85) |
| HO(4) | 13735 (75) | 34753 (28) | 44009 (115) | HC(63) | −46835 (96) | 15973 (182) | 44639 (99) |
| | | | | HO(2) | −38327 (49) | 10547 (60) | −6810 (61) |
| | | | | HO(3) | 5865 (40) | 53883 (57) | 707 (46) |
| | | | | HO(4) | 9194 (41) | 80561 (55) | 21593 (44) |

Table 3. *Least-squares fit to rigid-body motion for* β-L-*arabinose* (I), *and methyl* β-D-*xylopyranoside* (II)

The six atoms of the pyranose ring and the atoms O(1), O(2), O(3) and O(4) are also included.

| | (I) | (II) |
|---|---|---|
| $\langle$R.m.s. $|U_{ij} - U_{ij\,RBM}|\rangle$ | 0·0016 Å$^2$ | 0·0016 Å$^2$ |
| Max $|U_{ij} - U_{ij\,RBM}|$ | 0·0065 | 0·0044 |
| $\langle\sigma(U_{ij})\rangle$ | 0·0020 | 0·0019 |

Rigid-body **T** and $\omega$ elements and r.m.s. values for the principal axes of the **T** and $\omega$ tensors referred to the axes *a*, *b*, and *c* [*a*, *b*, and *c*\* for (II)]

| | (I) | | | (II) | | |
|---|---|---|---|---|---|---|
| **T** | 236 (8) | −32 (6) | 0 (7) (Å×10⁴) | 211 (8) | 14 (7) | −13 (8) (Å × 10⁴) |
| | | 175 (8) | −28 (8) | | 255 (8) | 17 (9) |
| | | | 176 (12) | | | 225 (10) |
| $\omega$ | 9·2 (1·4) | 1·7 (0·8) | −1·4 (0·8) (deg²) | 21·2 (1·3) | 14·3 (0·9) | −1·7 (0·7) (deg²) |
| | | 13·7 (1·3) | −0·1 (1·0) | | 16·9 (1·2) | 2·6 (0·8) |
| | | | 19·2 (0·9) | | | 11·9 (0·8) |

Direction relative to axes

| | R.m.s. values | | (I) | | | (II) | | |
|---|---|---|---|---|---|---|---|---|
| Tensor | (I) | (II) | a | b | c | a | b | c* |
| **T** | 0·159 Å | 0·162 Å | 152·9° | 64·7° | 99·1° | 81·2° | 23·1° | 68·8° |
| | 0·139 | 0·152 | 67·7 | 59·9 | 141·0 | 127·8 | 101·5 | 40·1 |
| | 0·119 | 0·140 | 104·6 | 138·8 | 127·5 | 39·1 | 109·8 | 57·8 |
| $\omega$ | 4·4° | 5·8° | 81·8° | 86·8° | 170·9° | 139·2° | 130·8° | 91·1° |
| | 3·8 | 3·6 | 107·2 | 161·8 | 95·6 | 76·4 | 104·2 | 160·2 |
| | 2·9 | 1·9 | 160·7 | 72·7 | 97·1 | 52·4 | 135·7 | 70·2 |

coordinates determined by Hordvik from his two-dimensional analysis. [This error had previously been reported from a packing-analysis study of the structure by Zugenmaier & Sarko (1972).] The variable parameters for all atoms and a scale factor, $k$, were refined together with the Zachariasen isotropic extinction parameter, $g$ (Coppens & Hamilton, 1970). The extinction correction, applied to $F_c^2$, was given by

$$E = \left[1 + \frac{2\bar{T}|F_c^2|g}{V^1 \sin 2\theta}\right]^{-1/2},$$

where $\bar{T}$ is the effective mean path length approximated from the calculated absorption, $A$, by $-(\ln A)/\mu$ and $V^1 = V^2/\lambda^3$. Some reflections were severely affected by the extinction in both analyses. For example, for the arabinose crystal, 002, 021 and 101 had $E$ values of 0·52, 0·46 and 0·49 respectively; for the methyl xyloside crystal, $E > 0·4 \leq 0·5$ for seven reflections. The final positional parameters for all atoms are listed in Table 2. The neutron scattering lengths used were $b_C = 0·6648 \times 10^{-12}$, $b_H = -0·3740 \times 10^{-12}$ and $b_O = 0·5803 \times 10^{-12}$ cm (Shull, 1972). The rigid-body-motion analysis was calculated (Schomaker & Trueblood, 1968) and results are reported in Tables 3 and 4. The atomic notation and thermal ellipsoids are shown in Figs. 1 and 2.*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32624 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. Thermal-motion corrections (Å) in β-L-arabinose (I) and methyl β-D-xylopyranoside (II) (Schomaker & Trueblood, 1968; Busing & Levy, 1964)

| | Rigid-body thermal motion* | | Minimum riding motion | | Riding motion | |
|---|---|---|---|---|---|---|
| | (I) | (II) | (I) | (II) | (I) | (II) |
| C–C | 0·007 (0·008) | 0·007 (0·008) | | | | |
| C–O | 0·006 (0·007) | 0·006 (0·007) | | | | |
| C–H(ring) | 0·004 (0·005) | 0·007 (0·009) | 0·004 | 0·006 | 0·025 | 0·027 |
| C–H(methyl)† | | 0·072 | | 0·024 | | 0·092 |
| O–H | | | 0·001 | 0·002 | 0·012 | 0·018 |
| O(4)–HO(4) | | | 0·007 | | 0·043 | |

* The values in parentheses also included the hydrogen atoms attached to the pyranose ring.
† Rigid-body motion for O–CH₃ group only.
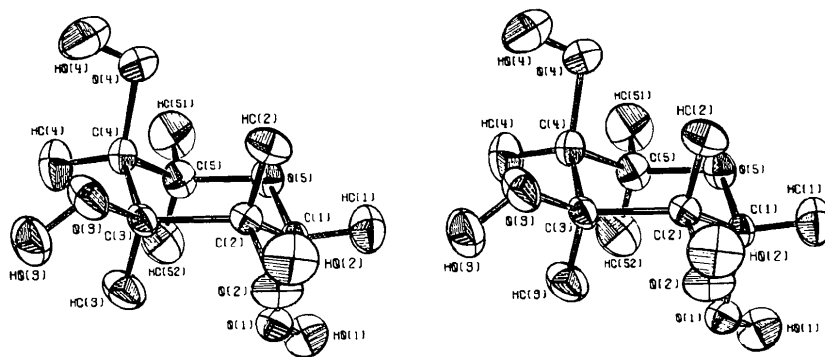


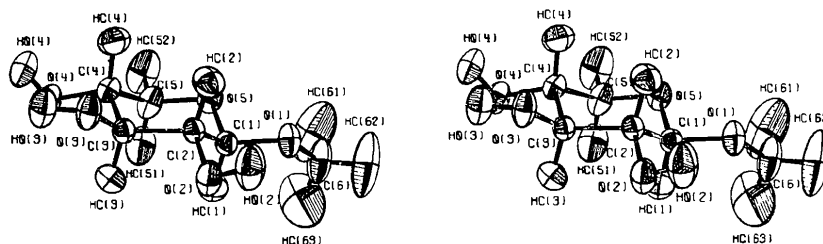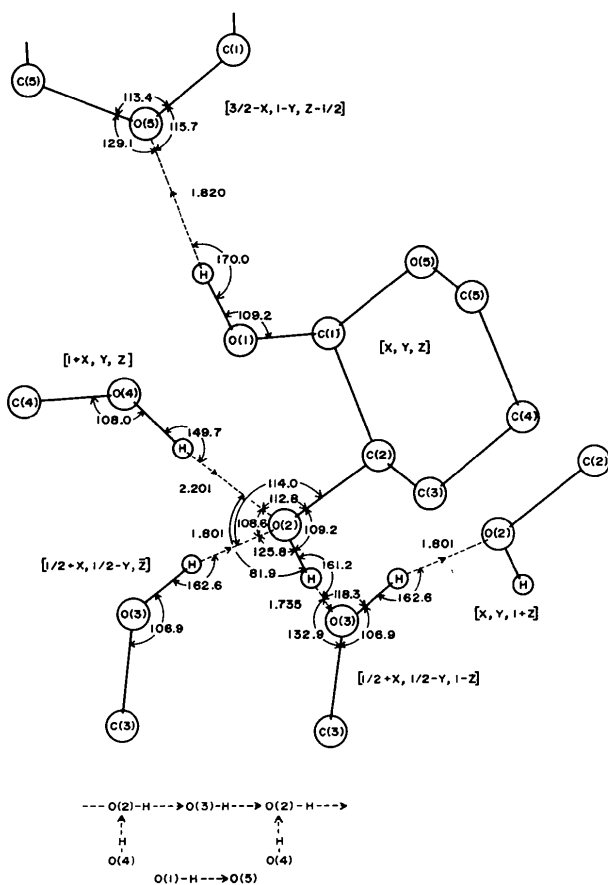Fig. 1. β-L-Arabinose: atomic notation and thermal ellipsoids at 50% probability (Johnson, 1976).
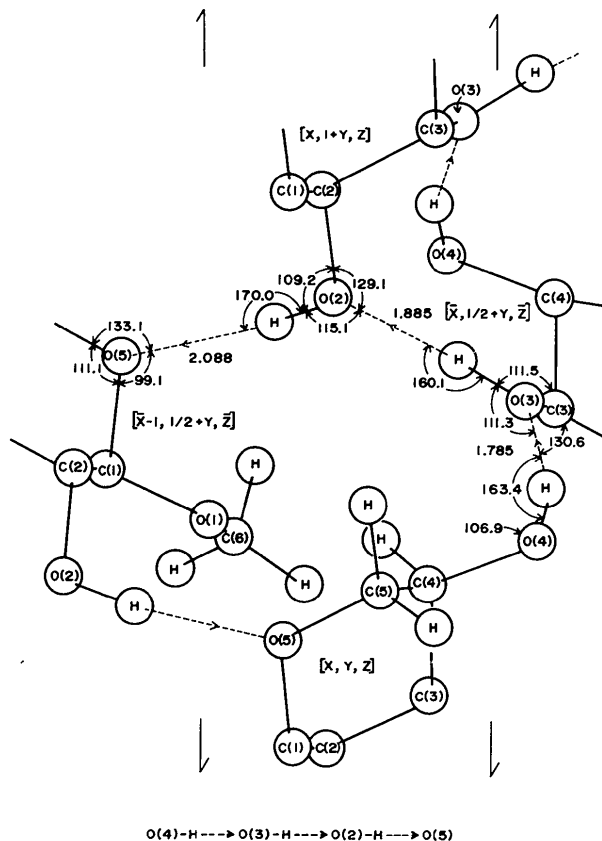


Fig. 2. Methyl β-D-xyloside: atomic notation and thermal ellipsoids at 50% probability (Johnson, 1976).

## Discussion

### The hydrogen bonding

The hydrogen-bond geometry of the two crystal structures is described in Table 5 and illustrated in Figs. 3 and 4. For the $\beta$-arabinose structure, it consists of infinite chains linking O(2)H and O(3)H, with a single-link branch from O(4)H to O(2). O(2) therefore donates one and accepts two hydrogen bonds, making an approximately tetrahedral coordination including the C—O bond. There are also separate links from the anomeric hydroxyl O(1)—H to the ring oxygen O(5).



Fig. 4. Methyl $\beta$-D-xyloside: hydrogen-bond geometry.



Fig. 3. $\beta$-L-Arabinose: hydrogen-bond geometry.

Except for the geometrical details, this scheme is the same as that deduced by Hordvik (1961) from his two-dimensional X-ray data.

The results from the $\beta$-arabinose structure show qualitative agreement with the relationship between bond type and bond distance observed by Jeffrey, Gress & Takagi (1977), but differ quantitatively. The two donor—acceptor H$\cdots$O bond lengths, O(2)H$\cdots$O(3) and O(3)H$\cdots$O(2), are shorter than that from the hydroxyl O(4)H, which has no hydrogen-bond acceptor function. The O(2)H$\cdots$O(3)H distance of 1·735 Å is at the extreme end of the range observed

Table 5. *Hydrogen-bonding geometry in $\beta$-L-arabinose* (I) *and methyl $\beta$-D-xylopyranoside* (II)

|      | Type of hydrogen bond | O—H | H$\cdots$O | $\angle$O—H$\cdots$O | O$\cdots$O |
|------|------------------------|-----------|-----------|------------|------------|
| (I)  | O(2)—H$\cdots$O(3)H | 0·974 (4) Å | 1·735 (4) Å | 161·2 (4)° | 2·680 (3) Å |
| (I)  | O(3)—H$\cdots$O(2)H | 0·975 (4) | 1·801 (4) | 162·6 (3) | 2·747 (3) |
| (II) | O(3)—H$\cdots$O(2)H | 0·969 (3) | 1·885 (3) | 160·1 (3) | 2·816 (2) |
| (II) | O(4)—H$\cdots$O(3)H | 0·969 (4) | 1·785 (4) | 163·4 (3) | 2·728 (2) |
| (I)  | O(4)—H$\cdots$O(2)H | 0·920 (6) | 2·201 (6) | 149·7 (5) | 3·032 (4) |
| (I)  | O(1)—H$\cdots$O(5) | 0·952 (4) | 1·820 (4) | 170·0 (4) | 2·762 (3) |
| (II) | O(2)—H$\cdots$O(5) | 0·962 (4) | 2·088 (4) | 170·0 (4) | 3·040 (3) |

(1·736–1·810 Å) for this type of interaction in the three methyl α-hexopyranosides (Jeffrey, McMullan & Takagi, 1977), but shorter ···OH···OH distances have been observed in carbohydrates, for example in D-glucitol (Park, Jeffrey & Hamilton, 1971). That the bond formed by the double-acceptor hydroxyl, O(2)H, would tend to be shorter than that with a single acceptor interaction, O(3)H, is consistent with the concept of the 'cooperative effect' in hydrogen bonding as defined by DelBene & Pople (1973).

The donor-only O(4)H···O(2) distance of 2·201 Å is much longer than the comparable bonds in the methyl hexopyranosides, and corresponds to a very weak interaction with a large deviation from O–H···O linearity of 150°. This geometry is similar to that of one of the bifurcated bonds in methyl α-D-altropyranoside (Poppleton, Jeffrey & Williams, 1975), but in this structure the next closest atoms to O(4)H are not oxygens, but C(4) and C(4)H at 1·917 and 2·144 Å respectively.

The hydrogen bond from the anomeric O(1)H to O(5) is shorter than the corresponding category in the methyl hexopyranosides and is shorter and more linear than the corresponding bond in α-D-glucose where the corresponding values are 1·914 Å and 161°. The anomeric hydroxyl does not accept a hydrogen bond, as predicted by Tse & Newton (1977).

In the methyl β-xyloside structure, the bond to the ring oxygen, O(2)H···O(5), is the longest, as would be expected, but the other two bond distances are reversed in that the donor-only bond O(4)–H···O(3) is shorter than the donor–acceptor bond O(3)–H··· O(2); it is also 3° closer to being linear. The linearity of the O–H···O geometry may be a factor which is comparable to that of 'cooperativity' in determining the strengths and lengths of hydrogen bonds. It is instructive, therefore, to examine these structures in more detail to attempt to identify the constraints which prevent these hydrogen bonds from being more linear.

In two cases the C–O–H valence angles are smaller than the usual value of 110 ± 1°: 106·9° for C(3)–O(3)–H in (I), and 106·9° for C(4)–O(4)–H in (II). In both cases the valence angles would have to be further decreased away from the tetrahedral angle in order to make the hydrogen bonds more linear.

In four cases the H–C–O–H torsion angles depart significantly from the ideal staggered value of 60°, which would be favored in the isolated molecule. These are H–C(2)–O(2)–H (20·7°), H–C(3)–O(3)–H (−21·0°), and H–C(4)–O(4)–H (27·7°) in (I), and H–C(4)–O(4)–H (−22·5°) in (II). To make the hydrogen bonds more linear would require that these torsion angles be made even smaller in every case, thereby increasing the eclipsing of these vicinal H atoms and, in consequence, their non-bonding repulsion interactions. It appears, therefore, that it is a combination of the other molecular packing forces and intramolecular constraints which distorts these hydro-

gen bonds from their optimum geometry with regard to bond length and linearity.

## The molecular dimensions

The dimensions of the molecules are illustrated in Figs. 5 and 6. The C–C bonds lie in the range between 1·518 and 1·530 Å, which is narrower (∼5σ) than is commonly observed in X-ray structure determinations of pyranose rings. The variations are, therefore, not
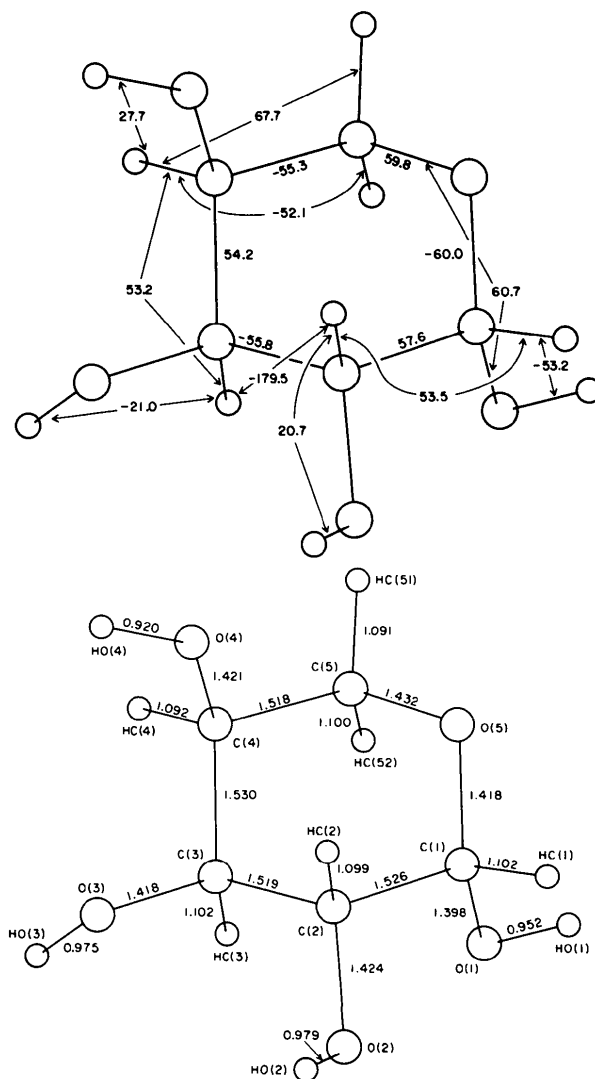


Fig. 5. Molecular dimensions of β-L-arabinose: torsion angles (°), bond lengths (Å), and bond angles (°). The standard deviations are as follows:

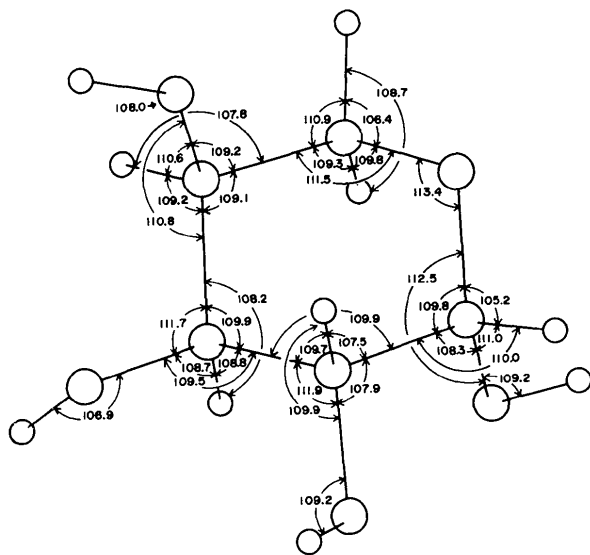| | | | |
|---|---|---|---|
| C/O–C/O–C/O–C/O | 0·2 ° | C–C | 0·002 Å |
| H–C–C/O–H | 0·4 | C–O | 0·003 |
| H–C(4)–O(4)–H | 0·6 | C–H | 0·004 |
| C/O–C/O–C/O | 0·2 | O–H | 0·004 |
| C–C/O–H | 0·3 | O(4)–H | 0·006. |
| H–C(5)–H | 0·3 | | |

Fig. 5 (cont.)

significantly different from the mean value of 1·5226 Å. With the exception of those in the acetal and hemiacetal sequence, the range in C—O bond lengths is also small, 1·416 to 1·424 Å (~3$\sigma$), and the variations are also not significantly different from the mean value of 1·4195 Å. The anomeric C(1)—O(1) bond length is short in both structures [1·398 Å in (I), 1·381 Å in (II)], which is consistent with the observations on other pyranose and methyl pyranoside molecules (Jeffrey & Takagi, 1977) and with theory (Jeffrey, Pople & Radom, 1974).

The C—H bond lengths range from 1·082 to 1·102 Å with a mean of 1·096 Å, for those of the methyl group. This is probably a thermal-motion effect, as shown by the corrections given in Table 4. Greater thermal motion, as a consequence of the very weak hydrogen bond, may also be responsible for the O(4)—H bond of 0·920 Å in $\beta$-arabinose, as compared with the mean value of 0·968 Å.

The pyranose ring is closer to an ideal $^4C_1$ chair in the arabinose molecule, as shown by the ring torsion angles and the Cremer & Pople (1975) puckering parameters, which are as follows: $\beta$-arabinose, $q_2 = 0·015$ Å, $q_3 = 0·572$ Å, $\varphi_2 = 116·3°$, $\theta = 1·5°$, $Q = 0·573$ Å; methyl $\beta$-xyloside, $q_2 = 0·082$ Å, $q_3 = 0·574$ Å, $\varphi_2 = 36·4°$, $\theta = 8·2°$, $Q = 0·580$ Å.

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Fig. 6. Molecular dimensions of $\beta$-D-xyloside: torsion angles (°), bond lengths (Å) and bond angles (°). The standard deviations are as follows:

| | | | |
|---|---|---|---|
| C/O–C/O–C/O–C/O | 0·2° | C–C | 0·002 Å |
| H–C–C/O–H | 0·4 | C–O | 0·002 |
| C/O–C/O–C/O | 0·1 | C–H | 0·003 |
| C–C/O–H | 0·3 | C–H (methyl) | 0·007 |
| H–C–H | 0·7 | O–H | 0·004. |

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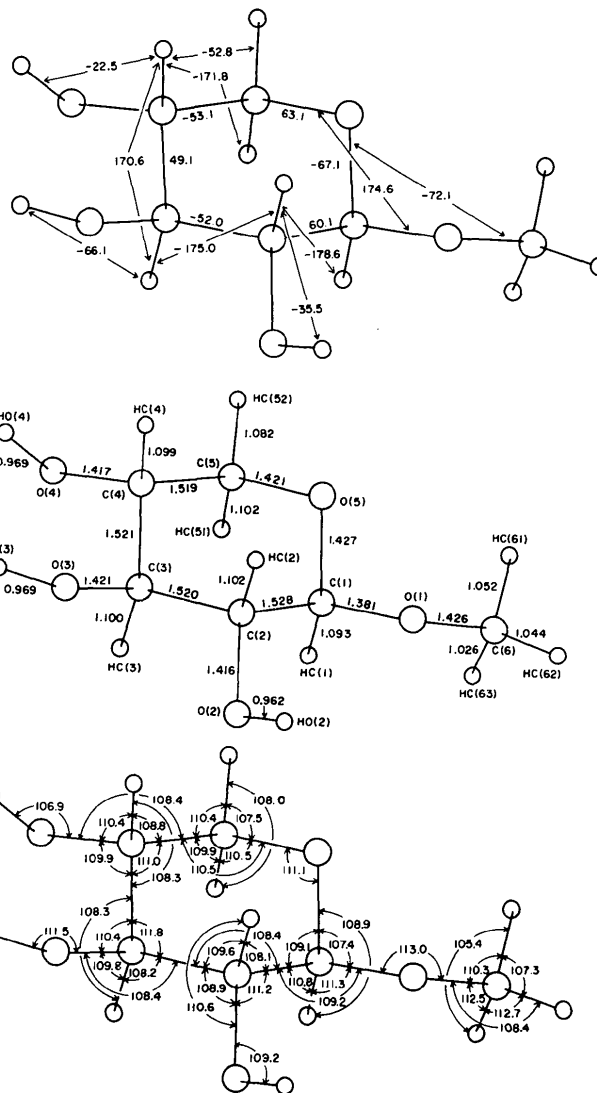
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# 2-Azanoradamantane N-Oxyl: The Phase Transition and the Crystallographic Structure of the Plastic Phase

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2-Azanoradamantane N-oxyl is an organic free radical nitroxide which is diamagnetic at room temperature. At 343 K it undergoes a reversible endothermic transition to a paramagnetic plastic phase; twinned face-centred cubic single crystals were obtained [$a = 9\cdot31$ (1) Å, $Z = 4$]. The crystallographic structure of this plastic phase was solved with the room-temperature molecular model and the relations between the low and the high-temperature cells. A molecular block-refinement program was used; the final $R$ value is $0\cdot085$ (31 observed structure factors and 3 variable parameters).

## Introduction

2-Azanoradamantane N-oxyl [which we shall henceforth call ANAO (Fig. 1)] is a nitroxide free radical which was synthetized at the Laboratoire de Chimie Organique Physique of the Centre d'Etudes Nucléaires de Grenoble (Dupeyre & Rassat, 1975). It crystallizes at room temperature in the form of pale-yellow volatile crystals of orthorhombic symmetry. In nitroxides the pale-yellow colour is characteristic of the existence of dimers due to the pairing of the electron spin localized on the N—O bonds. The pairing is confirmed by electron paramagnetic resonance studies (Decors, Genoud & Dupeyre, 1977) (the difference between the fundamental singlet and the triplet is of the order of 4000 K) and by the study of the crystallographic structure (Dupeyre & Capiomont, 1977).

At 343 K ANAO crystals undergo a reversible endothermic transition producing a plastic phase. The melting point cannot be observed as the product decomposes at about 423 K. It is the study of this
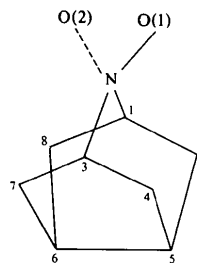


Fig. 1. Molecule of 2-azanoradamantane N-oxyl.