1,6-Anhydro-β-D-glucopyranose: Comparative Study of Two Independent Crystal Structure Determinations

K. BÖRJE LINDBERG

Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm, Sweden

The structure determination of 1,6-anhydro-β-D-glycopyranoside (levoglucosan) was originally performed, in attempts to correlate the molecular structure with acidity of two anhydropyranoses.[1] During this investigation a paper of Park, Kim and Jeffrey [2] describing the structure of levoglucosan was published. In their paper the hydrogen parameters was not refined, and the experimental conditions (wavelength of the radiation and diffractometer geometry) for the structure determination were different from what is described here. This paper gives a comparison between the two independent determinations by means of a half-normal probability plot[5] for the structural parameters.

Experimental. The cell dimensions were obtained from a powder photograph taken in a Guiner-Hägg focusing camera with strictly monochromatized Cu$K\alpha$I (λ = 1.54050 Å) radiation with KCl (a = 6.29428 Å) as an internal standard. A comparison of the unit cell dimensions from the two independent studies is given in Table 1. A sphere-shaped (r = 0.2 mm) single crystal was used and mounted parallel to the c-axis. Three-dimensional X-ray diffraction data were collected (ε-scan with varying interval and background intensity measured at each side) on a PAILRED single-crystal diffractometer with graphite monochromatized Mo$K\alpha$ radiation. The 896 independent data with $\sigma(I_{net})/I_{net} < 0.25$ were used in the subsequent calculations. The data were corrected for Lorentz and polarization effects.

Structure determination and refinement. The structure was solved by a computerized application of direct methods using the weighted phase-sum formula described by Norrestam.[3] Several cycles of full-matrix least squares refinement (anisotropic nonhydrogen and fixed anisotropic hydrogen thermal parameters, the same for the hydrogens as for the parent atoms) gave an R-value of 0.031. Hughes weighting scheme [4] was used with $|F_{min}| = 5.0$. The structural parameters are listed in Tables 2–3.

Table 1. Comparison of cell dimensions. Distances are given in Å.

Space group: $P2_12_12_1$ $Z = 4$

	This work	Park, Kim, and Jeffrey [2]
a	6.6866(7)	6.684(2)
b	13.295(2)	13.266(7)
c	7.542(9)	7.547(2)

Table 2. Fractional atomic coordinates in 1,6-anhydro-β-D-glucopyranose. Estimated standard deviations are given in parentheses.

	x	y	z
C(1)	0.1996(4)	0.0483(2)	0.3055(4)
C(2)	0.2545(3)	0.1316(2)	0.1755(3)
C(3)	0.0719(3)	0.1965(2)	0.1275(3)
C(4)	−0.0728(3)	0.2105(2)	0.2837(3)
C(5)	−0.0837(4)	0.1168(2)	0.3995(3)
C(6)	−0.1422(4)	0.0230(2)	0.2957(4)
O(1)	0.0471(3)	−0.0154(1)	0.2332(3)
O(2)	0.4139(3)	0.1898(1)	0.2463(2)
O(3)	−0.0275(3)	0.1493(1)	−0.0180(2)
O(4)	−0.0055(3)	0.2901(1)	0.3965(2)
O(5)	0.1150(3)	0.0907(1)	0.4589(2)
H(1)	0.312(4)	0.009(2)	0.340(4)
H(2)	0.294(4)	0.101(2)	0.065(3)
H(3)	0.117(4)	0.260(2)	0.094(3)
H(4)	−0.208(4)	0.221(2)	0.233(3)
H(5)	−0.159(4)	0.128(2)	0.503(3)
H(6a)	−0.202(4)	−0.023(2)	0.366(4)
H(6b)	−0.226(4)	0.040(2)	0.203(4)
H(O2)	0.398(5)	0.198(2)	0.342(4)
H(O3)	−0.046(5)	0.191(2)	−0.091(3)
H(O4)	−0.040(5)	0.335(2)	0.363(4)

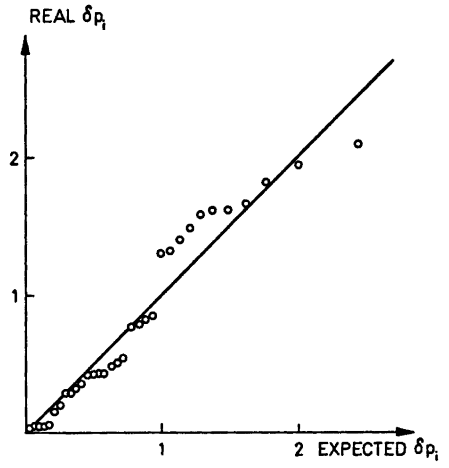

Fig. 1. Half-normal probability plot comparing results from Ref. 2 with this work.

Table 3. Anisotropic thermal parameters in 1,6-anhydro-β-D-glucopyranose. Estimated standard deviations are given in parentheses. The temperature factor expression used was exp $-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})$.

	$\beta_{11}\times 10^4$	$\beta_{22}\times 10^4$	$\beta_{33}\times 10^4$	$\beta_{12}\times 10^4$	$\beta_{13}\times 10^4$	$\beta_{23}\times 10^4$
C(1)	132(5)	23(1)	124(4)	12(2)	4(4)	11(2)
C(2)	98(4)	24(1)	73(3)	3(2)	7(3)	−3(2)
C(3)	106(4)	20(1)	75(3)	1(2)	−16(3)	4(2)
C(4)	92(4)	21(1)	90(3)	1(2)	−2(3)	−1(2)
C(5)	127(5)	22(1)	96(4)	−5(2)	37(4)	0(2)
C(6)	146(5)	26(1)	144(5)	−20(2)	23(4)	0(2)
O(1)	184(5)	20(1)	168(4)	−5(2)	35(4)	−14(2)
O(2)	111(3)	43(1)	79(2)	−15(2)	2(3)	7(2)
O(3)	184(4)	36(1)	84(3)	−9(2)	−50(3)	2(2)
O(4)	174(4)	20(1)	106(3)	7(2)	10(3)	−4(2)
O(5)	160(4)	29(1)	83(3)	4(2)	1(3)	11(2)

Comparison of the two independent structure determinations. Abrahams and Keve [5] have described how independent determinations of the same structure may be compared by means of a half-normal probability plot for the positional coordinates. A completely random distribution of errors leads to a linear plot of unit slope and zero intercept. Fig. 1 shows the half-normal probability plot between the positional parameters of this work and that of Park, Kim and Jeffrey.[2] Least squares of the positional parameter plot gives the values 1.05 ± 0.05 for the slope and -0.04 ± 0.05 for the intercept. The results indicate that the errors are mostly random, and the standard deviations of the positional parameters are likely to be correctly estimated.

However, the β_{ij} values are systematically lower in this work compared with those reported by Park *et al.*[2] In present work *c*-axis was chosen as the rotation axis and ω-scans were used. The need for larger detector aperture at high angle with this kind of scan compared with $\theta-2\theta$ scan together with the use of shorter wavelength makes it possible to explain the lower thermal parameters as caused by thermal diffuse scattering effects.[6,7]

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1. Lindberg, K. B., Lindberg, B. and Svensson S. *Acta Chem. Scand. 27* (1973) 373.
2. Park, Y. J., Kim, H. S. and Jeffrey, G. A. *Acta Crystallogr. Sect. B 27* (1971) 220.
3. Norrestam, R. *Acta Crystallogr. Sect. A 28* (1972) 303.
4. Hughes, E. W. *J. Amer. Chem. Soc. 63* (1941) 1737.
5. Abrahams, S. C. and Keve, E. T. *Acta Crystallogr. Sect. A 27* (1970) 157.
6. Burbank, R. D. *Acta Crystallogr. 17* (1964) 434.
7. Åsbrink, S. *Chem. Commun. (Univ. Stockholm)* (1973) No. XI.

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