& Boyd (1971). Further inspection of Fig. 2 suggests that the structure initially induced by the transition at 4800 kg cm^{-2} is not stable within the time scale of the X-ray exposure. For example the spacing of the (110) plane of the tetragonal structure at 4800 kg cm^{-2} still shows a little expansion with a further increase in pressure of 100 kg cm^{-2}, as compared with Fig. 1, where steady reduction of the (110) spacing is seen above 5000 kg cm^{-2}. In all these pressure regions, the (011) and (002) planes show steady decrease in spacing with increasing pressure and are more compressible than the (110) plane. Thus the crystal of adamantane after the transition is fairly anisotropic in the strains induced by hydrostatic pressures, being more compressible in the c direction than in the directions perpendicular to it. The strains are, however, isotropic before the transition, as shown by the cubic structure sustained under pressure (Fig. 1). The unit-cell dimension of the cubic structure just before the pressure transition is $a = 9\cdot20$ Å (at 4600 kg cm^{-2}) and the calculated volumetric strain of the crystal at this stage is 6·9%.

It is worth while to note that at p_t and 20°C, the crystal transition in adamantane arises in such a way that one of the original cubic axes shrinks 4·2% and becomes parallel to the tetragonal c axis, while both of the other two axes *expand* 0·5% in the tetragonal [110] and [$\bar{1}$10] directions (numerical values were calculated at two pressures, 4600 and 5000 kg cm^{-2}). The net effect is an abrupt volumetric contraction of 3·1%, which corresponds to abrupt molecular rearrangements toward denser packing.

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The crystal structure of α-D-glucose monohydrate.

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The crystal structure of α-D-glucose monohydrate has been refined with intensity data measured diffractometrically, using the coordinates from the photographic study of Killean, Ferrier & Young [*Acta Cryst.* (1962). **15**, 911]. The final R index is 0·0301 for 906 statistically significant reflexions.

Introduction

The determination of the crystal structure of α-D-glucose monohydrate has been previously reported by Killean, Ferrier & Young (1962). Their study was based on visual estimation of Weissenberg photographs, and their model refined to an R of 0·17. This communication reports an accurate re-refinement using intensities estimated diffractometrically.

Experimental

A single crystal kindly supplied by Dr R. C. G. Killean was used. Data were collected on an off-line Siemens automatic diffractometer, with the crystal mounted about the a axis. The compound crystallizes in the space group $P2_1$, with lattice constants $a = 8\cdot803$ (1), $b = 5\cdot085$ (1), $c = 9\cdot708$ (2) Å, and $\beta = 97\cdot67$ (1)°. Intensity data were collected using a five-value measuring technique (Allen, Rogers & Troughton, 1971), to a limit of 70° in θ, using Cu $K\alpha$ radiation. 915 independent reflexions were recorded, of which 906 had intensities significantly greater than background [$I > 2\cdot58\sigma(I)$].

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Structure refinement

Least-squares refinement was started with the coordinates of Killean *et al.* for the carbon and oxygen atoms, which were refined anisotropically. The positions of the hydrogen atoms were deduced from difference maps, and refined with isotropic temperature factors. The scattering factors used for carbon and oxygen were those published by Cromer & Waber (1965), and for hydrogen those given by Stewart,

Table 1. *Final positional parameters for the non-hydrogen atoms* ($\times 10^4$), *as fractions of the unit-cell edges*

Standard deviations are in parentheses.

	x	y	z
C(1)	1891 (3)	1372	700 (3)
C(2)	1088 (3)	14 (6)	1783 (3)
C(3)	1942 (3)	308 (7)	3245 (2)
C(4)	3611 (3)	−458 (6)	3235 (3)
C(5)	4322 (3)	1058 (6)	2142 (3)
C(6)	5959 (3)	296 (8)	2033 (3)
O(1)	1814 (2)	4128 (5)	858 (2)
O(2)	−467 (2)	833 (5)	1686 (2)
O(3)	1227 (2)	−1425 (5)	4112 (2)
O(4)	4442 (2)	96 (5)	4578 (2)
O(5)	3450 (2)	544 (5)	792 (2)
O(6)	6133 (2)	−2493 (5)	1870 (2)
O(7)	−1179 (2)	−4750 (5)	3217 (2)

Table 2. *Final anisotropic thermal parameters* ($\times 10^4$) *for the non-hydrogen atoms, with standard deviations in parentheses*

The thermal parameters are of the form: $\exp\left(-2\pi^2 \sum_i \sum_j U_{ij}h_ih_ja_i^*a_j^*\right)$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	234 (12)	323 (16)	231 (13)	51 (13)	10 (10)	−28 (13)
C(2)	202 (11)	296 (17)	240 (12)	−2 (12)	22 (10)	−68 (13)
C(3)	237 (12)	295 (15)	202 (11)	−11 (14)	38 (9)	−22 (13)
C(4)	263 (13)	245 (15)	194 (11)	8 (12)	−19 (10)	−17 (11)
C(5)	216 (12)	255 (15)	246 (13)	−5 (12)	13 (10)	1 (12)
C(6)	218 (12)	388 (18)	397 (15)	3 (15)	41 (11)	7 (17)
O(1)	428 (11)	236 (11)	301 (10)	61 (10)	−16 (8)	16 (10)
O(2)	186 (8)	387 (14)	364 (10)	30 (10)	15 (7)	−136 (11)
O(3)	414 (11)	520 (16)	207 (9)	−160 (12)	84 (8)	−24 (11)
O(4)	361 (10)	370 (12)	249 (9)	−2 (11)	−96 (7)	−35 (11)
O(5)	237 (8)	338 (12)	185 (8)	36 (10)	50 (7)	−5 (10)
O(6)	301 (10)	453 (14)	323 (10)	128 (11)	46 (8)	−37 (11)
O(7)	305 (9)	308 (11)	313 (9)	1 (11)	43 (8)	37 (11)

Davidson & Simpson (1965). Without making allowance for dispersion by the carbon and oxygen atoms, refinement converged at $R = 0.0301$. The effects of allowing for dispersion in this structure have been reported earlier (Neidle & Rogers, 1970). A table of the observed and calculated structure factors has been deposited with the National Lending Library as Supplementary Publication No. SUP 30025.* Tables 1–3 give the final atomic parameters. The strong low-order reflexions 001, 0Ī1 and 10Ī were omitted from the refinement because of suspected extinction effects.

Table 3. *Final positional and isotropic thermal parameters for the hydrogen atoms* ($\times 10^3$)

	x	y	z	$U(\text{Å}^2)$
H(1)—C(1)	144 (3)	98 (6)	−26 (3)	18 (6)
H(2)—C(2)	109 (3)	−186 (6)	158 (2)	12 (6)
H(3)—C(3)	193 (4)	239 (8)	352 (3)	10 (8)
H(4)—C(4)	368 (3)	−229 (6)	301 (3)	13 (6)
H(5)—C(5)	430 (3)	303 (7)	243 (3)	4 (7)
H(6)—C(6)	635 (3)	119 (7)	119 (3)	3 (8)
H(7)—C(6)	654 (3)	80 (8)	290 (3)	8 (8)
H(8)—O(1)	167 (4)	465 (8)	6 (3)	23 (10)
H(9)—O(2)	−51 (3)	223 (8)	199 (3)	9 (9)
H(10)-O(3)	129 (4)	−117 (9)	491 (4)	28 (11)
H(11)-O(4)	493 (5)	−133 (10)	488 (5)	35 (11)
H(12)-O(6)	599 (4)	−284 (10)	94 (4)	33 (12)
H(13)-O(7)	−193 (5)	−415 (12)	293 (4)	62 (16)
H(14)-O(7)	−51 (5)	−363 (11)	331 (4)	51 (14)

$\langle$C–H$\rangle = 1.01$ (8) Å
$\langle$O–H$\rangle = 0.82$ (9) Å

Discussion

Table 4 lists the non-hydrogen bond lengths and angles; the atomic numbering scheme used is shown in Fig. 1. The absolute configuration shown is that determined previously (Neidle & Rogers, 1970).

There are significant differences between the molecular dimensions reported here, and those found in the study of Killean *et al.* For example, bond C(1)–O(1) is of length 1·412 Å, compared with 1·38 Å, and C(6)–O(6) is now 1·438 Å instead of 1·46 Å.

* Copies of the table may be obtained through the Exec utive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Bond lengths and angles for the non-hydrogen atoms, with estimated standard deviations in parentheses*

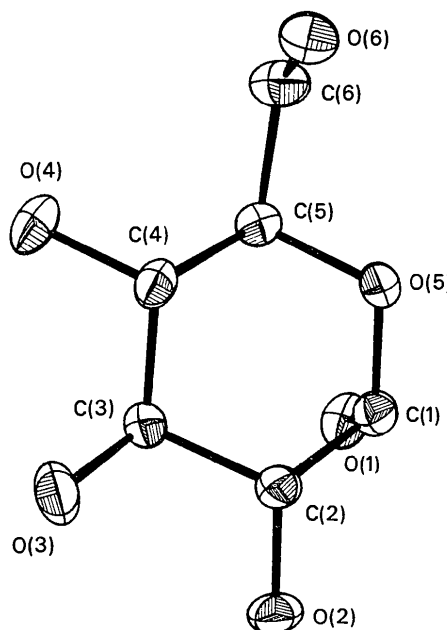|			
C(1)–C(2)	1·509 (3) Å	C(2)–C(1)–O(1)	110·2 (2)°
C(1)–O(1)	1·412 (2)	C(2)–C(1)–O(5)	110·9 (2)
C(1)–O(5)	1·427 (3)	O(1)–C(1)–O(5)	110·2 (2)
C(2)–C(3)	1·522 (3)	C(1)–C(2)–C(3)	112·7 (2)
C(2)–O(2)	1·422 (3)	C(1)–C(2)–O(2)	110·9 (2)
C(3)–C(4)	1·521 (3)	C(3)–C(2)–O(2)	112·6 (2)
C(3)–O(3)	1·422 (4)	C(2)–C(3)–C(4)	109·0 (2)
C(4)–C(5)	1·513 (4)	C(2)–C(3)–O(3)	106·8 (2)
C(4)–O(4)	1·435 (3)	C(4)–C(3)–O(3)	110·5 (2)
C(5)–C(6)	1·510 (4)	C(3)–C(4)–C(5)	111·4 (2)
C(5)–O(5)	1·451 (3)	C(3)–C(4)–O(4)	108·7 (2)
C(6)–O(6)	1·438 (5)	C(5)–C(4)–O(4)	109·2 (2)
		C(4)–C(5)–C(6)	114·0 (2)
		C(4)–C(5)–O(5)	108·9 (2)
		C(6)–C(5)–O(5)	106·6 (2)
		C(5)–C(6)–O(6)	112·2 (2)
		C(1)–O(5)–C(5)	113·1 (2)

Fig. 1. (010) projection of a molecule of α-D-glucose mono-hydrate. The thermal ellipsoids are scaled to include 50% probability.

The mean carbon–carbon bond length of 1·515 Å compares well with that of 1·518 Å in α-D-glucose–urea adduct (Snyder & Rosenstein, 1971), and that of 1·524 Å (with spread of 0·021 Å), quoted by Strahs (1970) in his review of carbohydrate crystal structures. The carbon–oxygen bond lengths show significant variations; thus C(1)–O(5) and C(5)–O(5) differ by 0·024 Å, 8σ. This C(1)–O(5)–C(5) situation is paralleled in many pyranose-ring carbohydrates, with O(5)–C(5) always longer by 0·02–0·03 Å; in the α-D-glucose–urea adduct (Snyder & Rosenstein, 1971) the difference is 0·029 (4) Å. The α-D-glucose ring in raffinose pentahydrate (Berman, 1970) has a difference of 0·014 (8) Å, and α-rhamnose monohydrate has one of 0·022 (3) Å (Killean, Lawrence & Sharma, 1971).

Excluding C(1)–O(5), C(5)–O(5) and C(1)–O(1) (which is slightly short), the other carbon–oxygen bonds have an average length of 1·429 Å, with a standard deviation of 0·007 Å. Strahs quotes an average of 1·425 Å, with a spread of 0·016 Å.

The dimensions reported here strengthen the conclusion of Strahs that there is no ideal or uniform average bond dimension for carbohydrates, probably because of the distorting effects of the extensive hydrogen bonding in the crystal lattice.

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Structure cristalline de Gaδ. Par L. Bosio, H. Curien,* M. Dupont et A. Rimsky,* *Groupe de Recherche 'Physique des Liquides et Electrochimie' du C.N.R.S., associé à l'Université Paris VI, 9 Quai St Bernard, Paris 5ème, France*

Supercooled liquid gallium can crystallize in the metastable δ-form at atmospheric pressure. A crystallographic study on monocrystals and powders has shown that δ-Ga has the space group $R\bar{3}m$ with $a = 7·729$ Å and $α = 72°02'$. The rhombohedral unit cell contains 22 atoms distributed on five independent special sites.

Des mesures thermiques différentielles effectuées à la pression atmosphérique ou à haute pression et des mesures de supraconductibilité ont montré que, dans certaines conditions, des échantillons de gallium de faible masse pouvaient cristalliser dans une forme distincte de celles déjà connues: Gaα (Bradley, 1935), Gaβ (Bosio, Defrain, Curien & Rimsky, 1969), Gaγ (Bosio, Curien, Dupont & Rimsky, 1972). Cette variété, Gaδ, métastable à la pression atmosphérique, fond à 253,7 K. L'étude cristallographique de cette phase solide a été effectuée en réalisant des clichés de diffraction des rayons X sur des monocristaux de masse voisine du milligramme et sur des poudres constituées de particules de 1 à 10 μm de diamètre.

L'orientation quelconque du monocristal formé dans la chambre de diffraction nécessite l'emploi d'une méthode déjà utilisée pour l'étude des autres phases métastables du

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gallium: sur les deux moitiés d'un même film cylindrique, on réalise successivement avec le même monocristal un diagramme de cristal tournant et un diagramme de Weissenberg à partir desquels on peut construire une projection cotée du réseau réciproque. Les diagrammes relatifs à deux échantillons monocristallins ont été ainsi obtenus: les quelques deux cents taches de diffraction qu'ils contenaient ont été indexées et les paramètres de la maille déterminés avec une précision de 2%. Afin de vérifier ces résultats et affiner les paramètres, plusieurs diagrammes de poudre ont été réalisés dans une chambre de Debye–Scherrer (Bosio, Defrain & Dupont, 1971) et sur un diffractomètre $θ–θ$ à largeur de fente variable.

L'ensemble de ces mesures montre que la variété Gaδ est rhomboédrique; à $191 ± 2$ K, les paramètres affinés par une méthode de moindres carrés sont:

$a = 7,729 ± 0,004$ Å et $α = 72°02' ± 03'$ dans la description rhomboédrique et $A = 9,087 ± 0,006$ Å, $C = 17,02 ± 0,01$ Å dans la description hexagonale.

Tableau 1. *Coordonnées atomiques et facteur d'agitation thermique de* Gaδ

	x	y	z	β
Ga(1)	0	0	0	1,0 ± 0,6
Ga(2)	½	0	0	1,9 ± 0,6
Ga(3)	0,1735 ± 0,0008	0,347 ± 0,002	0,7304 ± 0,0009	1,1 ± 0,3
Ga(4)	0,101 ± 0,001	0,202 ± 0,002	0,1771 ± 0,0008	1,7 ± 0,3
Ga(5)	0,101 ± 0,001	0,201 ± 0,002	0,5770 ± 0,0008	1,2 ± 0,3