shows large discrepancies for the C—N bond and O lone-pair densities.

The mean phase differences $|\overline{\Delta\varphi}|$ between $F_{o,x}$ and $F_{c,N}$ vary with $|F|$ more sharply than was found by Thomas (1978) for lithium formate monohydrate. For urea, the maximum value of 1·47° occurs for low $|F|$ values and $|\overline{\Delta\varphi}|$ decreases with increasing $|F|$. With $\sin\theta/\lambda$, $|\overline{\Delta\varphi}|$ has a peak at about 0·5 Å^{-1} and falls off at lower and higher angles.

Thomas (1978) has compared (X–N) and deformation refinement procedures and discussed the advantages of the latter, particularly for non-centrosymmetric cases, in terms of the problem of phases discussed above.

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Rigid-Body Coordinates of Pyranose Rings

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Abstract

161 published structures containing pyranose rings, listed in the Cambridge Crystallographic Data File, have been investigated to establish the orthogonal coordinates of the average ring. Details are given of the mathematical procedures used in the calculations, of the results for the various hexoses, and of variations found.

Introduction

In crystallographic structural work, it is often advantageous to be able to treat a group of atoms as a rigid body, *i.e.* a group in which the atoms maintain a constant relationship to each other in terms of the distances between the atoms and the angles between interatomic vectors, when the whole group of atoms is rotated about any axis or translated in any direction. Two examples may be given. In the calculation of the overall scattering curve for use with direct methods of crystallographic phase-angle determination, the inclusion of a known rigid group, in terms of a molecular scattering factor, in place of the equivalent number of atomic scattering factors, can improve the accuracy of the scale-factor determination and the unitary scattering factors and hence produce more reliable phase angles. Secondly, if the number of independent parameters in a structure determination, *e.g.* positional and thermal vibration parameters, is large compared with the number of independent observational parameters, then the introduction of a group of atoms, treated as a rigid body, can be used to reduce the number of structural parameters to be refined. In this case, the $3n$ positional parameters of n atoms are replaced by six parameters for the rigid body consisting of three positional and three rotational parameters.

These advantages require that the specification of the atoms of the rigid group is an accurate representation of the group involved and, though it is usually possible to calculate the dimensions of such a group from known values of bond lengths and angles, other factors may make slight, but significant, differences from the calculated model.

One method of establishing the most accurate representation of a particular group is to examine previously determined structures which contain that group and, from these known conformations, derive the atom parameters which give the best least-squares fit. Care must be taken, however, to ensure that the

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comparison structures do not contain examples which are distorted by chemical forces exerted by attached groups or strong crystal-packing forces or have systematic errors, arising from a variety of sources, in the published coordinates. This point will be referred to later.

A suitable group for investigation is the pyranose ring of the saccharides, as the results of a large number of crystal-structure determinations involving such rings have been published. From these accumulated data it is possible to derive an accurate specification for the pyranose ring and, in addition, to check what variations occur (*a*) between the rings of the various hexoses and (*b*) between these and the rings of non-hexoses which also exist in the pyranose form, *e.g.* xylose, fructose.

The data base for such an investigation is available at the Cambridge Crystallographic Data Centre (CCDC) (Allen *et al.*, 1979) which maintains a computer file of organic and organometallic crystal structures (Kennard, Watson, Allen, Motherwell, Town & Rogers, 1975). In addition to the lists of atomic coordinates and other data, computer programs are available to carry out searches for specific molecules or fragments of molecules (Murray-Rust & Motherwell, 1978).

Mathematical operations

As the atom coordinates of a crystal structure are usually published as fractional coordinates, *i.e.* as a fraction of the appropriate cell edge in cells which may have non-orthogonal angles, the first requirement is to convert all atom coordinates into lengths of the same units along a chosen set of orthogonal axes. This conversion to orthogonal axes may be carried out by a separate computer program if required, but the CCDC system includes a routine to produce such coordinates and will also set the specified group of atoms in a fixed orientation relative to the orthogonal axes if three atoms are defined to be set in turn at:

(*a*) the origin;
(*b*) along the x axis;
(*c*) in the xy plane, not collinear with the first two.

For the pyranose ring these have been specified as O(1), C(1) and C(3) respectively. Examination of the resulting coordinate sets allows the occurrence of mirror images or other systematic variations from the normal arrangement to be identified and, if it is intended to use these coordinates in the analysis, the necessary corrections can be made, *e.g.* L forms are reflected across the xy plane.

For the final arrangement of the pyranose-ring atoms, it was decided to rotate the molecule about the x axis until C(2) and C(4) had the same z coordinate, as shown in Fig. 1.

If the chair form of the ring were fully symmetrical, this arrangement would then give:

$$y[\mathrm{C}(2)] = -y[\mathrm{C}(4)];$$
$$y[\mathrm{C}(1)] = -y[\mathrm{C}(5)];$$
$$z[\mathrm{C}(1)] = z[\mathrm{C}(5)] = -z[\mathrm{C}(2)] = -z[\mathrm{C}(4)];$$

and hence departures from ideal symmetry are obvious. However, as the atoms bonded to C(5) and C(1) are usually different types, ideal symmetry is unlikely. From the coordinates listed in the data file it is a simple operation to rotate the group until C(3) lies on the x axis (this could have been specified in the original listing) and then rotate about the x axis until either C(2) has the same z coordinate as the theoretical model or C(2) and C(4) have equal z coordinates. In practice, the first alternative has been implemented with the usual methods of vector algebra to establish the angle of rotation and the direction of rotation, though if, as in this case, the required rotation is always in the same direction, the calculation may not be required. Rotation through the required angle α is then carried out with a rotation matrix derived from Euler's equations of transformation:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} l^2\beta + \cos\alpha & ml\beta - n\sin\alpha & nl\beta + m\sin\alpha \\ lm\beta + n\sin\alpha & m^2\beta + \cos\alpha & nm\beta - l\sin\alpha \\ ln\beta - m\sin\alpha & mn\beta + l\sin\alpha & n^2\beta + \cos\alpha \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix},$$

where l,m,n are the direction cosines of the rotation axis and $\beta = 1 - \cos\alpha$ (Mirsky, 1963).

The second rotation, about the x axis, is calculated in a similar manner with vectors perpendicular to the rotation axis passing through the same atom, *e.g.* C(2), in the observed and calculated groups.

It remains to adjust the orientation of each observed group of atoms to give the best least-squares fit with the calculated (or average) group. Two iterative procedures are involved. Each set of observed data has to be shifted and rotated to fit the reference group of atoms and then the whole process is repeated, with the calculated average, until no changes in the calculated parameters are observed. As the average is unknown until the calculation has been carried out at least once we may start with either a selected group, thought to be fairly near the average, or a calculated set of values. In

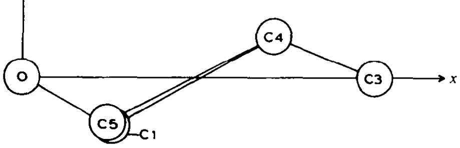

Fig. 1. Diagram showing the standard orientation of the pyranose rings after rotation and translation.

addition, each atom should be treated similarly unless a specific weighting system is in use, and hence the centre of gravity, invariant for a fixed group, is used as the origin about which any rotations are carried out. The first step in the process of fitting is thus to shift the observed and calculated groups so that the centre of gravity of each is the origin.

We now require to calculate the three rotations α, β and γ about x, y and z respectively, which will make the sum of the squares of the differences between the coordinates of the calculated and observed groups a minimum. The standard matrix for a rotation through an angle α about x is

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{bmatrix},$$

but, if the angle α is small, we may use the approximations $\cos\alpha \simeq 1$ and $\sin\alpha \simeq \alpha$ and the rotation matrix becomes

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & -\alpha \\ 0 & \alpha & 1 \end{bmatrix}.$$

Similarly, if β and γ are small, then their rotation matrices may be approximated to

$$\begin{bmatrix} 1 & 0 & \beta \\ 0 & 1 & 0 \\ -\beta & 0 & 1 \end{bmatrix} \quad \text{and} \quad \begin{bmatrix} 1 & -\gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

Multiplication of these matrices together, in any order, gives the product

$$\begin{bmatrix} 1 & -\gamma & \beta \\ \gamma & 1 & -\alpha \\ -\beta & \alpha & 1 \end{bmatrix},$$

which provides the equations relating the original coordinates, x,y,z, with the rotated coordinates, x',y',z':

$$x' - x = \Delta x = -y\gamma + z\beta;$$

$$y' - y = \Delta y = x\gamma - z\alpha;$$

$$z' - z = \Delta z = -x\beta + y\alpha;$$

from which the required values of α, β and γ can be calculated by least squares.

The calculated angles must be used in the rotation matrices which contain the full trigonometrical functions to avoid distortion of the rigid group. After the rotations have been carried out, the total variance $[V_{\text{tot}} = \sum(\Delta x)^2 + \sum(\Delta y)^2 + \sum(\Delta z)^2]$ may be calculated as a measure of the goodness-of-fit.

The process may then be repeated and iteration continued until there is no further change in V_{tot} or until the calculated rotation angles are all less than a previously specified value. Iteration is necessary as any coordinate is affected by either of two rotations and the errors are large when the rotation angles are large. The errors decrease as the calculated angles decrease in size and the process is found to converge quite rapidly, rarely needing more than three cycles. Once this process of fitting has been carried out for all the groups in the list, a new calculated group can be derived as the (weighted) average of the observed groups and a new cycle carried out. This second, overall, iteration is repeated until there is no change in the calculated value. Obviously, if an observed group is removed from the calculation, for any reason, then the overall iteration must be repeated.

A computer program has been written, in Algol 68, to carry out the iterative fittings described above, and the results obtained for the various pyranose rings are presented below.

Results

Fragments with the required configuration were retrieved by the *CONNSER* specification shown in Table 1. Stereoisomers are not separated by this routine and, hence, a subroutine was used in the iteration program to check for L forms of the ring and, when found, to convert to the D form by reflection. From the data file of May 1979 containing 21 248 entries, 161 references were retrieved which provided 216 rings, some of the entries referring to compounds containing more than one ring. No sets of coordinates were removed at this stage, even if they were flagged as error sets. Only 189 sets of coordinates were available.

Separation into the eight monosaccharides was next carried out, usually by reference to the title of the compound as listed by *BIBSER*, though in some cases it was necessary to refer to the original paper when the

Table 1. *Retrieval of fragments with the required configuration*

Q PYRANOSE				Title
AT1	O	2		type specifications
AT2	C	3		
AT3	C	3		
AT4	C	3		
AT5	C	3		
AT6	C	3		
BO	1	2	1	connectivity specifications
BO	2	3	1	
BO	3	4	1	
BO	4	5	1	
BO	5	6	1	
BO	6	1	1	
NOCS				
END				

Table 2. *Final situation for the eight pyranoses*

Pyranose	Number used	Number not used	Average $V_{tot} \times 10^4$	$\bar{\sigma} \times 10^4$	Average standard deviation $\times 10^4$ x	y	z
Allose	2	0	10	–	–	–	–
Altrose	3	0	7	–	–	–	–
Glucose	111	16	90	56	173	168	299
Mannose	12	1	105	87	180	192	307
Gulose	3	0	89	–	–	–	–
Idose	2	0	42	–	–	–	–
Galactose	32	4	42	25	129	117	197
Talose	3	0	55	–	–	–	–
Glu, Man, Gal	155	21	81·3	52·0	164·5	159·3	278·6

title was insufficient. Each group was then iterated, first against a calculated ring, and then against the average produced. At this point it was possible to specify which sets gave particularly bad fits to the average, due to various factors, *e.g.* if two hydroxyl groups are linked to form an additional ring then the sugar ring is distorted. In order to obtain a clear indication of the relative fit between an observed set of coordinates and the average ring, the value of the total variance (V_{tot}) was listed for each comparison. At the end of the complete set of iterations, the average V_{tot} and the standard deviation were calculated and the difference between each V_{tot} and the average divided by the standard deviation. Sets which differed from the average by more than three standard deviations were removed and the reduced set reiterated. Any additional

Table 3. *Reference codes and coordinates of the average ring for allose*

Allose
Structures used
ALTRCA
ALTRCA

O(5)	0·000 (4)	0·000 (7)	0·000 (19)
C(1)	0·638 (2)	1·214 (4)	−0·260 (7)
C(2)	2·042 (3)	1·251 (1)	0·331 (8)
C(3)	2·850 (2)	0·000 (11)	0·000 (2)
C(4)	2·039 (11)	−1·242 (4)	0·331 (3)
C(5)	0·702 (1)	−1·199 (2)	−0·388 (14)

Table 4. *Reference codes and coordinates of the average ring for altrose*

Altrose
Structures used
MALTPY
MALTPYO1
PACALP

O(5)	0·000 (3)	0·000 (6)	0·000 (1)
C(1)	0·656 (4)	1·207 (2)	−0·312 (10)
C(2)	2·062 (4)	1·263 (12)	0·269 (5)
C(3)	2·873 (2)	0·000 (5)	0·000 (12)
C(4)	2·045 (8)	−1·248 (9)	0·269 (1)
C(5)	0·702 (1)	−1·178 (4)	−0·437 (3)

Table 5. *Reference codes and coordinates of the average ring for glucose*

Glucose
Structures used

ABCMHP
ABGPON
ACCELL10
ACCELL10
ACCELL10
ACELLO
ACELLO
ACGLUA10
ACGLUA11
ACHITM10
ACHITM10
AGLCAM
ANTAMA
ANTAMA
ANTBRN
APTERN
BAVTEX
BLACTO
CASDIN
CELLOBO1
CELLOBO1
CELLOBO2
CELLOBO2
CHONDM
CYTSAC
CYTSAC
DDGLPY
DECGPY10
DIPIDE10
DMCLCM10
DPGXHT
GLPMAC10
GLUAMB
GLUAMB01
GLUAMC
GLUAMC11
GLUBRP

GLUCMH
GLUCMH11
GLUCSA
GLUCSE
GLUCSE01
GLUCUR20
GURXPX10
IMATUL
KESTOS
KGLUCD
KGLUCP
KMYRMH01
KMYRMH10
LACBCB
LACCCB
LACTCC10
LACTOS01
LACTOS10
LAMBIO
LAMBIO
LONOTL
MALTOS10
MALTOS10
MALTOS11
MALTOS11
MALTOT
MALTOT
MAMSGP
MASCAR10
MBDGPH10
MCELOB
MCELOB
MELEZT01
MELEZT01
MELIBM01
MELIBM02
MELIBM10

MGLUCP
MGLUCP11
MHALAM
MMALTS
MMALTS
MOAGLP10
MSUGLU
MTAGLV
MXFGPY
NABDGC
NAPAGQ
NPGAMM
PAUCIN
PHMALT
PHMALT
PHMALT
PHMALT
PLANTE10
RAFINO
SGLOLR
SUCROS03
SUCROS04
SUCROS11
TAGPBR
TAGPEX
TAGPOX10
TLANTB
TRECAB
TREHAL01
TREHAL01
TREHAL02
TREHAL02
TREHAL03
TREHAL03
TREHAL10
TREHAL10
TURANS

Not used

CAGLUC10
ANTBRN
ANTINA
CARRTL
CELLOB
CELLOB
DATSIB10
IPMALT
IPMALT
MHALAM
PAFLEB
ANTINA
GLPHYC10
GLULAC10
LONOTL
RGLUCD

O(5)	0·000 (12)	0·000 (18)	0·000 (31)
C(1)	0·682 (23)	1·188 (15)	−0·379 (25)
C(2)	2·033 (14)	1·248 (19)	0·323 (28)
C(3)	2·850 (13)	0·000 (16)	0·000 (28)
C(4)	2·045 (20)	−1·251 (16)	0·323 (37)
C(5)	0·689 (22)	−1·200 (17)	−0·383 (30)

bad fits were removed and so on until the remaining sets were all acceptable on the above basis. A final check involved a re-run with all sets included, to check if modification of the average by the later removals had any effect on the acceptability of earlier removals. In cases of doubt, a possible re-entry was tested alone with the accepted set, and usually rejected.

Table 2 shows the final situation for the eight pyranoses in terms of the number of data sets used and rejected, the average total variance, standard deviation of the total variances and the average standard deviations of the x, y and z coordinates for those pyranoses with more than five examples.

In addition, for each pyranose, Tables 3 to 10 list the reference codes produced by the search routine divided, where applicable, into those used and those not used, and the coordinates of the average ring as calculated, in Å. The standard deviations, where given, are derived from the distribution of the observed sets around the average values and not from the e.s.d.'s of the published coordinates. No weighting has been applied except that acceptance or rejection may be regarded as weights of 1 and 0 respectively.

An overall average ring was calculated from each of the individual pyranose average rings, weighted by the number of sets of data used to produce them, and the coordinates are presented in Table 11. The deviations of the individual pyranose rings from the overall average ring are shown in the diagrams of Fig. 2, where the average ring is shown, together with a vector on each atom which represents the difference from the average of each pyranose multiplied by a suitable scale factor for clarity. Table 12 lists the specified torsion angles for each of the eight pyranose rings.

Table 6. *Reference codes and coordinates of the average ring for mannose*

Mannose Structures used			Not used
MBDDAC78	AMPIAB10	TAMANC	DMANPR10
ADITSM	MEMANP	TAMCUR	
ADMANN	MEMANP11	TBZMAC	
ADMANN	NACMAN10	XFMANP	

O(5)	0·000 (14)	0·000 (15)	0·000 (26)
C(1)	0·673 (24)	1·198 (17)	−0·318 (44)
C(2)	2·051 (18)	1·253 (19)	0·335 (40)
C(3)	2·858 (9)	0·000 (22)	0·000 (19)
C(4)	2·067 (20)	−1·235 (17)	0·335 (27)
C(5)	0·716 (21)	−1·206 (25)	−0·356 (28)

Table 7. *Reference codes and coordinates of the average ring for gulose*

Gulose Structures used	BNOVCM BDGHEP PACDGP		
O(5)	0·000 (3)	0·000 (2)	0·000 (50)
C(1)	0·668 (18)	1·204 (26)	−0·322 (19)
C(2)	2·053 (11)	1·244 (2)	0·317 (37)
C(3)	2·862 (11)	0·000 (8)	0·000 (26)
C(4)	2·052 (9)	−1·248 (10)	0·317 (14)
C(5)	0·696 (18)	−1·206 (37)	−0·363 (24)

Table 8. *Reference codes and coordinates of the average ring for idose*

Idose Structures used	MABIDP PAIDOP		
O(5)	0·000 (12)	0·000 (1)	0·000 (16)
C(1)	0·654 (17)	1·187 (1)	−0·356 (26)
C(2)	2·041 (6)	1·262 (18)	0·268 (39)
C(3)	2·860 (8)	0·000 (5)	0·000 (20)
C(4)	2·047 (1)	−1·250 (11)	0·268 (1)
C(5)	0·678 (14)	−1·197 (3)	−0·400 (10)

Table 9. *Reference codes and coordinates of the average ring for galactose*

Galactose Structures used			Not used
ACYGAP	CANAGL01	MCDGAL	CBFUCS
ADGALA01	CANAGL10	MEAGPY	HCEREB
ADGALA10	CHONDM	MELIBM01	SRHXGU
AGALAM01	DMGALP	MELIBM02	FUSICO10
AGALAM10	HCEREB	MELIBM10	
BDGALA	LACCCB	MGALBH	
BDGALA	LACTCC10	MGALPY	
BDGLOS01	LACTOS10	PLANTE10	
BDGLOS10	MAGALP10	RAFINO	
BLACTO	MBDGAL	SRGALU	
CAGALA10	MBDGAL01		

O(5)	0·000 (10)	0·000 (11)	0·000 (19)
C(1)	0·692 (14)	1·193 (11)	−0·372 (20)
C(2)	2·042 (13)	1·246 (11)	0·324 (20)
C(3)	2·848 (12)	0·000 (12)	0·000 (20)
C(4)	2·051 (14)	−1·260 (12)	0·324 (24)
C(5)	0·701 (14)	−1·192 (13)	−0·389 (16)

Table 10. *Reference codes and coordinates of the average ring for talose*

Talose Structures used	ADTALO01 ADTALO10 DATALP		
O(5)	0·000 (17)	0·000 (13)	0·000 (24)
C(1)	0·697 (22)	1·194 (10)	−0·361 (2)
C(2)	2·043 (2)	1·244 (11)	0·350 (20)
C(3)	2·846 (12)	0·000 (2)	0·000 (10)
C(4)	2·036 (18)	−1·253 (4)	0·350 (36)
C(5)	0·688 (34)	−1·210 (4)	−0·383 (17)

Discussion

The first point worthy of note is the severe imbalance of the numbers of structures available for the eight pyranoses; only three, glucose, galactose and mannose, have more than three determinations listed. Glucose alone accounts for approximately 72% of the list and hence dominates the calculation of the overall average

Table 11. *Coordinates of the overall average ring*

O(5)	0·000 (11)	0·000 (16)	0·000 (28)
C(1)	0·682 (21)	1·190 (14)	−0·370 (24)
C(2)	2·038 (13)	1·248 (17)	0·323 (27)
C(3)	2·851 (12)	0·000 (15)	0·000 (25)
C(4)	2·048 (18)	−1·251 (15)	0·323 (32)
C(5)	0·694 (20)	−1·199 (16)	−0·383 (26)

ring. The coordinates for all eight have, however, been presented as a record of the information available at present, though the following comments are based mainly on the details of the three more numerous rings.

Deviations from a six-membered ring in the chair form, calculated by simple geometry on the basis of accepted bond lengths and angles, are produced by several causes, some of which are (*a*) the presence of the O atom in the ring (*b*) different atoms bonded to C(1) and C(5) and (*c*) different arrangements of atoms on the remaining C atoms.

The average bond angle in the ring at the C atoms is 110·2° but the angle at the O atom is 113·4°. This would tend to splay out C(1) and C(5), but this is outweighed by the shorter bond lengths between C and O atoms compared with the normal C—C single bond, and the net result is that C(1) and C(5) are about 4·5% closer to each other than C(2) and C(4).

As C(1) is attached to an O atom and C(5) is (usually) attached to a C atom, there may be specific effects due to this difference to account for the fact that the *z* coordinates of C(1) and C(5) are not equal, but, as the calculations carried out have not distinguished between α and β forms, it is not possible to establish any details.

There remain the effects due to the variations of the other three O atoms [on C(2), C(3) and C(4)]. Some of these variations are shown by the differences between the average of a specific pyranose ring and either the overall average or other average rings. These effects, plus the forces due to the high degree of hydrogen bonding, may result in a tendency to flatten the ring (Strahs, 1970). A crude measure of this effect is the O(5) to C(3) distance, though a more accurate function would include all three diagonal distances. The clearest indication of variations of the ring geometry is given by

ALLOSE

GULOSE

ALTROSE

IDOSE

GLUCOSE

GALACTOSE

MANNOSE

TALOSE

Fig. 2. Stereopairs showing the average pyranose ring (large circles) with vectors for the named pyranoses (small circles) corresponding to the differences from the average. The difference vectors are multiplied by the following scalars: allose × 10; altrose × 10; glucose × 100; mannose × 20; gulose × 20; idose × 20; galactose × 50; talose × 20.

Table 12. *Torsion angles for average pyranose rings* (°)

	Allose	Altrose	Glucose	Mannose	Gulose	Idose	Galactose	Talose
O(5)–C(1)–C(2)–C(3)	48·12	47·90	56·63	53·01	52·10	51·21	56·30	57·18
C(1)–C(2)–C(3)–C(4)	−50·05	−45·07	−53·61	−52·69	−51·03	−46·61	−53·78	−55·81
C(2)–C(3)–C(4)–C(5)	55·21	50·29	53·66	54·68	52·74	48·72	53·83	56·63
C(3)–C(4)–C(5)–O(5)	−57·85	−57·68	−56·43	−56·11	−55·14	−54·24	−56·99	−57·75
C(4)–C(5)–O(5)–C(1)	58·96	62·20	62·05	58·25	58·51	60·96	62·42	61·81
C(5)–O(5)–C(1)–C(2)	−53·76	−57·27	−62·21	−56·84	−56·70	−59·81	−61·66	−61·86

a comparison of the standard deviations of the coordinates, from which it appears that the σ's of the z coordinates (the z axis is only a few degrees away from being perpendicular to the least-squares best plane of the ring) are, on average, 1·7 times the σ's of the x and y coordinates, which have σ's similar to each other.

Examination of the variations due to axial or equatorial O atoms has not given any clear indication of a systematic effect on the coordinates due to the different directions of these atoms.

Conclusion

The average coordinates have been presented for the pyranose-sugar ring atoms, for each pyranose sugar and for an overall average ring, based on crystal structures listed in the Cambridge Crystallographic Data File dated May 1979 by a least-squares iterative refinement of the fixed groups. The results show variations between pyranose rings, though qualified by the meagre number of samples of five of the pyranoses and, within each ring, a difference between the standard deviation of the z coordinates and the standard deviations of the x and y coordinates in the specified orientation.

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A Short Hydrogen Bond between Near Identical Carboxyl Groups in the α Modification of L-Glutamic Acid

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Abstract

The structure of the α modification of L-glutamic acid, $C_5H_9NO_4$, has been determined from neutron diffraction data using direct methods. The space group is $P2_12_12_1$ with a = 10·282 (10), b = 8·779 (8), c = 7·068 (7) Å and Z = 8 and the final R value is 0·026 for 1160 observations. As in the β modification of the compound a short hydrogen bond with an O···O length of 2·58 Å was found between the two carboxyl groups. The location of the H atom in the bond is explained from acid–base considerations, and the shortness of the bond is accounted for using bond-length–bond-strength considerations. The conformation of the side chain containing the δ-carboxyl group differs considerably in the two modifications, showing this part of the molecule to be highly flexible.

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