The Crystal Structure of Uridine*

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Crystals of uridine, $C_9H_{12}N_2O_6$, are monoclinic, space group $P2_1$ with $a = 4.981$ (4), $b = 14.649$ (8), $c = 13.964$ (8) Å, $\beta = 95.45$ (8)° and $Z = 4$. The structure was solved by the direct method and refined by least-squares calculations, using Ni-filtered Cu $K\alpha$ diffractometer data. The final R index was 0.033 for 2232 reflections, and the standard deviations in the atomic positions are about 0.003 Å. The two independent molecules have very similar conformations; the conformation about the glycosidic bond is *anti*, the sugar ring is puckered with $C(3')$ *endo*, and the conformation about $C(4')-C(5')$ is *gauche–gauche*.

Introduction

Crystal structure studies of uridine were undertaken concurrently by two independent groups, one at Pittsburgh and the other at Caltech. For both groups, interest in the study was sparked by the presence of two molecules in the asymmetric unit, and by the hope that a knowledge of the detailed crystal structure would lead to further study of the relationship between intermolecular forces and intramolecular geometry. The solution and initial refinement of the structure were based on data collected at Pittsburgh; final refinement was based on data collected at Caltech.

Structure determination and initial refinement (Pittsburgh)

Crystals were initially obtained by the slow evaporation at room temperature of an equimolar solution of uridine and chloroamphenicol in ethanol. Identical crystals were later obtained from a solution of 150 mg of uridine in 25 ml of ethanol which was maintained at 37°C for 5–10 days. The crystals obtained by either procedure were clear, brittle platelets with principal faces {010} and elongated along **a**.

The crystal density was measured by flotation in a solution of iodobenzene and carbon tetrachloride. Lattice parameters and intensities were measured on a Picker FACS-1 automated diffractometer equipped with a graphite monochromating crystal. The space group $P2_1$ was indicated by the systematic absence of

reflections $0k0$ with k odd. Crystal data are summarized in Table 1.

Table 1. *Crystal data*

Uridine	$C_9H_{12}N_2O_6$
Monoclinic	F.W. 244.2
Space group $P2_1$	$Z = 4$
$a = 4.981$ (4) Å	$F(000) = 512$
$b = 14.649$ (8)	$D_x = 1.597$ g cm^{-3}
$c = 13.964$ (8)	$\mu(Cu\ K\alpha) = 11.9$ cm^{-1}
$\beta = 95.45$ (8)°	$\mu(Mo\ K\alpha) = 1.47$ cm^{-1}

Two sets of intensity data were collected from the same crystal, estimated to be $0.3 \times 0.08 \times 0.08$ mm. The first, which was used in the solution of the structure, was collected with Cu $K\alpha$ radiation, a scan width of 1.5°, a scan rate of 2° min^{-1}, and background counts of 10 s. Of the 1796 reflections surveyed to $\sin \theta/\lambda = 0.59$, all but 27 had net intensities greater than 2σ above background. The second data set was collected with Mo $K\alpha$ radiation, a scan width of 1.2°, a scan rate of 1° min^{-1}, and 20 s background counts. Of the 2899 reflections surveyed out to $\sin \theta/\lambda = 0.75$, 925 had intensities less than 2σ above background. Observational variances included counting statistics plus a 'lack-of-confidence' term $(0.05S)^2$ where S is the scan count (Peterson & Levy, 1957).

The structure was solved by the direct method using the DP5 phase extension and tangent refinement program (Hall, 1967). The origin was specified by assigning phase angles of zero to the $\overline{1}06$, 101 and 114 reflections ($E = 2.47$, 1.98 and 1.81). The 130 reflection, $E = 2.08$, was chosen to define the enantiomorph. The best value for its phase angle was found to be $0.65\ \pi$ by 'multiple solution' (trial-and-error) between $\pi/4$ and $3\pi/4$, using the residual error index $R' = \sum ||E_o| - |E_c||/\sum |E_o|$ as the criterion. Four additional reflections, 260, 4,12,0,

2,0,14, and 0,16,6 $(E = 2\cdot29, 1\cdot57, 1\cdot97$ and $1\cdot52)$ were assigned phase angles on the basis of strongly consistent indications during preliminary cycles of tangent refinement. With these eight reflections constituting a starting set, tangent refinement and expansion gave an $R' = 0\cdot17$, indicating a correct solution. The conventional residual error index $R = \sum||F_o| - |F_c||/\sum|F_o|$ was $0\cdot18$ for the first set of structure factors calculated from the atomic positions picked out of the resulting E synthesis, with appropriate change in enantiomorph.

Initial refinement at Pittsburgh based on the data set collected with Cu $K\alpha$ radiation converged to an R index of $0\cdot10$ for the heavy atoms only; the difference map, however, failed to reveal the positions of the hydrogen atoms. The results have been summarized elsewhere (Green, Shiono, Rosenstein & Abraham, 1971). The second set of data was then collected with Mo $K\alpha$ radiation. Three difference maps, interspersed with block-diagonal and partial-matrix least-squares refinement, indicated the positions of all 24 hydrogen atoms and led to an R index of $0\cdot058$, without correction for extinction.

At this time, the Pittsburgh and Caltech groups became aware of their duplication of efforts; the Caltech group had not been successful in their attempts at deriving a satisfactory structure, but their experimental data appeared to be more accurate and accordingly final refinement was carried out at Caltech.

Structure refinement (Caltech)

Intensity data were initially collected in 1967, but a structure solution was not obtained. The structure refinement reported here is based on data collected in 1970. The crystal used for data collection was an approximately square prism, about $0\cdot2 \times 0\cdot2 \times 0\cdot4$ mm, elongated in the **b** direction. Intensities were measured on a Datex-automated* General Electric diffractometer, with Ni-filtered Cu $K\alpha$ radiation, a scintillation counter and pulse-height discriminator, and a θ–2θ scan mode with background counts of 30 s. Two

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* Total counts accumulated over complete scan collected in discrete steps of $0\cdot01°$ in 2θ.

Table 2. *Coordinates and anisotropic thermal parameters for the heavy atoms*

All values are multiplied by 10^4. The thermal parameters are of the form $\exp(-2\pi^2)(h^2a^{*2}U_{11}\ldots + 2klb^*c^*U_{23})$.

Molecule A

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	6405 (4)	1210 (1)	3174 (1)	306 (11)	248 (10)	255 (9)	−29 (9)	44 (8)	18 (8)
C(2)	8031 (5)	1476 (2)	2481 (2)	349 (14)	256 (12)	273 (12)	−10 (11)	59 (10)	43 (10)
N(3)	9747 (4)	2187 (1)	2730 (1)	358 (12)	274 (10)	271 (9)	−56 (9)	94 (9)	31 (8)
C(4)	10126 (5)	2607 (2)	3623 (2)	376 (14)	266 (12)	308 (12)	6 (11)	22 (10)	4 (10)
C(5)	8367 (5)	2292 (2)	4298 (2)	473 (16)	322 (13)	274 (12)	−39 (13)	87 (11)	−27 (10)
C(6)	6608 (5)	1627 (2)	4056 (2)	395 (15)	301 (13)	280 (12)	−22 (11)	124 (11)	8 (9)
O(2)	7945 (4)	1093 (1)	1697 (1)	571 (13)	391 (10)	253 (8)	−144 (10)	116 (8)	−42 (8)
O(4)	11861 (4)	3203 (1)	3774 (1)	481 (12)	403 (11)	398 (10)	−196 (10)	82 (9)	−35 (8)
C(1')	4522 (5)	428 (2)	2938 (2)	293 (12)	307 (12)	262 (11)	−57 (11)	16 (9)	29 (10)
C(2')	5980 (5)	−490 (2)	3031 (2)	330 (13)	274 (12)	264 (11)	−54 (10)	67 (10)	−31 (9)
C(3')	5821 (5)	−686 (2)	4098 (2)	273 (12)	279 (12)	274 (11)	−6 (10)	25 (10)	−12 (9)
C(4')	3005 (5)	−359 (2)	4247 (2)	265 (12)	249 (11)	297 (12)	−32 (10)	20 (10)	13 (9)
O(1')	2571 (3)	421 (1)	3610 (1)	243 (9)	306 (9)	357 (9)	18 (8)	67 (7)	71 (7)
C(5')	2545 (5)	−110 (2)	5269 (2)	373 (14)	337 (13)	337 (13)	−60 (12)	106 (11)	−25 (10)
O(2')	4464 (4)	−1163 (1)	2486 (1)	632 (14)	370 (10)	319 (9)	−200 (10)	114 (9)	−104 (8)
O(3')	6282 (4)	−1611 (1)	4340 (1)	550 (12)	267 (9)	342 (9)	116 (9)	86 (9)	32 (7)
O(5')	4664 (4)	436 (1)	5702 (1)	458 (11)	403 (10)	324 (9)	−68 (9)	77 (8)	−108 (8)

Molecule B

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	8354 (4)	4845 (1)	1199 (1)	385 (12)	255 (10)	283 (10)	−41 (9)	112 (9)	−53 (8)
C(2)	8089 (6)	4191 (2)	499 (2)	623 (20)	288 (13)	368 (14)	−110 (13)	217 (14)	−79 (11)
N(3)	6324 (5)	3501 (2)	650 (2)	721 (18)	382 (12)	362 (12)	−244 (12)	256 (12)	−154 (10)
C(4)	4838 (5)	3396 (2)	1423 (2)	372 (14)	325 (13)	327 (13)	−30 (12)	98 (11)	22 (11)
C(5)	5242 (5)	4098 (2)	2122 (2)	419 (15)	347 (13)	289 (12)	−15 (12)	145 (11)	2 (10)
C(6)	6956 (5)	4778 (2)	1994 (2)	486 (16)	329 (13)	305 (12)	−27 (13)	148 (12)	−80 (11)
O(2)	9328 (5)	4218 (1)	−211 (1)	1154 (21)	438 (12)	568 (14)	−372 (13)	603 (15)	−237 (10)
O(4)	3366 (4)	2725 (1)	1450 (1)	666 (14)	454 (12)	442 (11)	−298 (11)	226 (10)	−79 (9)
C(1')	10297 (5)	5593 (2)	1074 (2)	343 (14)	255 (12)	304 (12)	−27 (10)	84 (10)	−47 (10)
C(2')	9069 (5)	6399 (2)	485 (2)	394 (15)	316 (12)	265 (12)	−65 (12)	48 (10)	11 (10)
C(3')	8199 (5)	7008 (2)	1286 (2)	308 (13)	299 (12)	273 (11)	−19 (10)	60 (10)	27 (9)
C(4')	10579 (5)	6900 (2)	2046 (2)	308 (13)	224 (11)	331 (12)	−15 (10)	75 (10)	−8 (10)
O(1')	11255 (3)	5937 (1)	1988 (1)	386 (10)	246 (9)	334 (9)	21 (8)	−31 (8)	−31 (7)
C(5')	10114 (5)	7140 (2)	3061 (2)	331 (14)	389 (14)	339 (13)	−36 (12)	36 (11)	−63 (11)
O(2')	11163 (4)	6857 (1)	59 (1)	612 (13)	370 (10)	322 (9)	−75 (10)	239 (9)	−6 (8)
O(3')	7532 (4)	7925 (1)	1045 (1)	476 (12)	303 (9)	396 (10)	78 (9)	133 (9)	83 (8)
O(5')	7536 (4)	6851 (1)	3311 (1)	436 (11)	302 (9)	369 (9)	−39 (8)	180 (8)	−15 (8)

sets of data were collected out to $\sin \theta/\lambda = 0.63$ Å^{-1}, one at a scan speed of $1°$ min^{-1} and the second at a rate of $2°$ min^{-1}. Two check reflections (135 and $\overline{1}94$) were monitored continually; they showed no significant intensity change. Observational variances $\sigma^2(I)$ were based on counting statistics plus a lack-of-confidence factor of 2% estimated error in the experiment. One reflection, 101, was assigned zero weight because of a large disparity between the two measurements; the remaining 2232 recorded reflections – including 10 with averaged net intensities less than zero – were included in the least-squares refinement.

The starting parameters were furnished by the Pittsburgh group. Ultimately, they were partitioned among four matrices; one contained the C, N and O coordinates of molecule A, the C, N and O coordinates of molecule B were in a second, the coordinates and isotropic temperature parameters of all 24 hydrogen atoms were in a third, and the scale factor, a secondary extinction parameter [Larson, 1967; equation (3)] and

the anisotropic temperature parameters of the 34 heavier atoms in the fourth. In this approximation, all y parameters were refined. The quantity minimized was $\sum w(F_o^2 - F_c^2)^2$, with weights w equal to $\sigma^{-2}(F_o^2)$. Form factors for C, N and O were from *International Tables for X-ray Crystallography* (1962); for H, from Stewart, Davidson & Simpson (1965). No correction was made for anomalous dispersion or absorption. Convergence was accepted when no parameter shifted by more than 0.5σ and the 'goodness-of-fit' $[\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ was 2·30. Final parameters are given in Tables 2 and 3; the final value of the secondary extinction coefficient g was 19·0 (0·7) $\times$ 10^{-6}.*
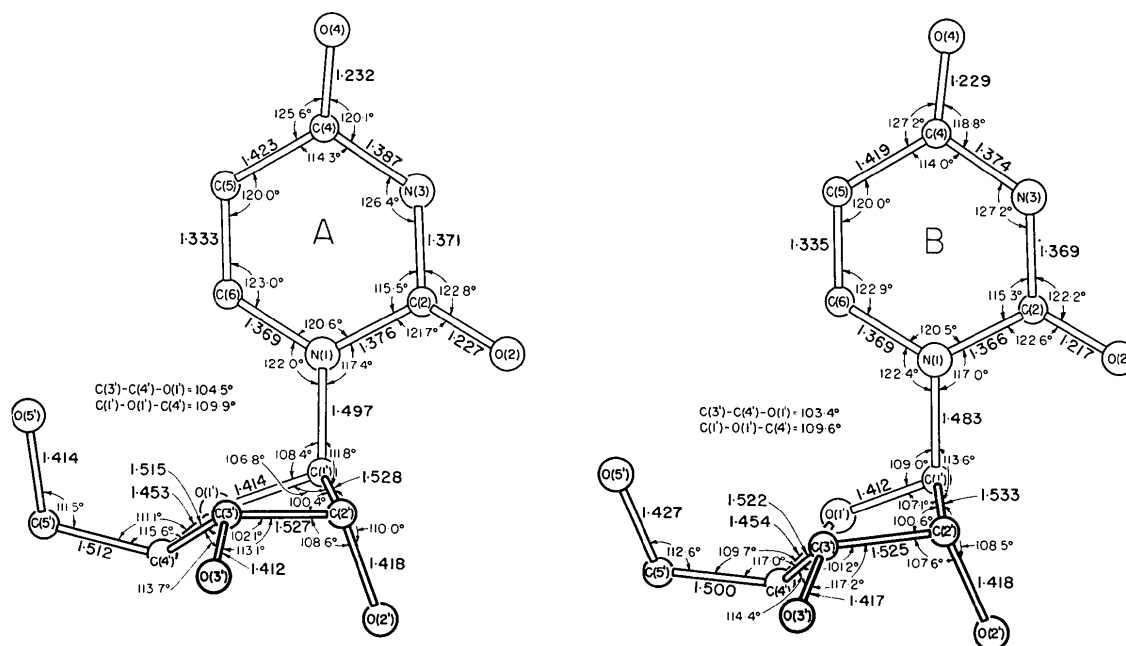

Fig. 1. Bond distances and angles involving the heavy atoms.

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

	Molecule A				Molecule B			
	x	y	z	B	x	y	z	B
H(1)	1080 (6)	241 (2)	226 (2)	4·4 (0·7)	605 (6)	313 (2)	20 (2)	5·4 (0·8)
H(2)	855 (5)	255 (2)	493 (2)	2·7 (0·5)	433 (6)	407 (2)	267 (2)	3·9 (0·6)
H(3)	531 (5)	138 (2)	450 (2)	2·5 (0·5)	718 (6)	528 (2)	241 (2)	3·7 (0·6)
H(4)	364 (5)	50 (2)	364 (5)	2·3 (0·5)	1176 (5)	531 (2)	75 (2)	2·2 (0·5)
H(5)	788 (5)	−44 (2)	284 (2)	2·5 (0·5)	761 (5)	616 (2)	−2 (2)	3·1 (0·6)
H(6)	544 (7)	−125 (2)	197 (2)	8·3 (0·9)	1126 (6)	661 (2)	−47 (2)	6·1 (0·8)
H(7)	714 (5)	−32 (2)	449 (2)	2·5 (0·5)	663 (5)	673 (1)	153 (1)	1·8 (0·5)
H(8)	684 (7)	−167 (2)	496 (2)	4·2 (1·0)	888 (6)	816 (2)	72 (2)	3·7 (0·7)
H(9)	180 (2)	−82 (2)	402 (2)	1·4 (0·5)	1213 (5)	728 (2)	189 (2)	1·8 (0·5)
H(10)	248 (5)	−71 (2)	563 (2)	2·8 (0·6)	1019 (6)	782 (2)	314 (2)	4·0 (0·6)
H(11)	83 (6)	20 (2)	528 (2)	3·9 (0·7)	1150 (6)	686 (2)	351 (2)	4·4 (0·7)
H(12)	407 (6)	81 (2)	609 (2)	5·4 (0·8)	678 (7)	735 (2)	363 (2)	6·2 (0·8)

Results and discussion

Bond distances and angles involving the heavy atoms, as calculated from the Caltech parameters given in Table 2, are shown in Fig. 1. The formal standard deviations in the distances are in the range 0·003–0·004 Å. On the other hand, the r.m.s. value of the 18 differences between corresponding distances in the two independent molecules is 0·0075 Å, suggesting that the standard deviation in a single value is actually about 0·005 Å. This discrepancy is not unusual, and in the present case may be blamed in part on the separation of the parameters into four different matrices.

It is somewhat interesting to note that the bond distances calculated from the Pittsburgh refinement, and which have e.s.d.'s in the range 0·005–0·007 Å, show the same pattern of discrepancies between molecules A and B; indeed, the r.m.s. value of the 36 differences between the Pittsburgh and Caltech bond

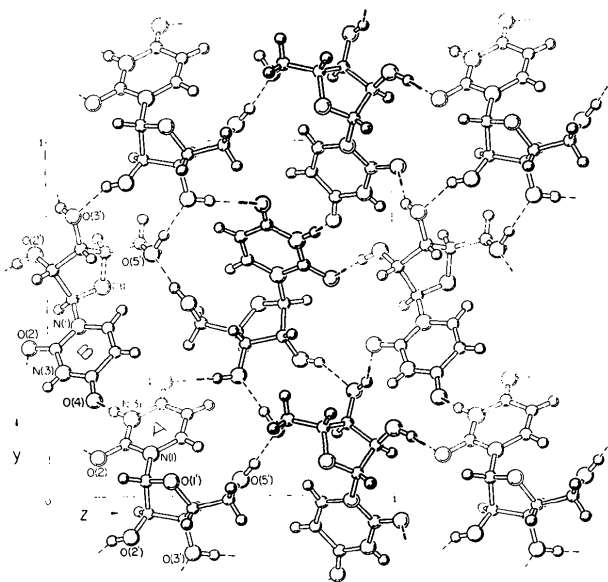Fig. 2. The crystal structure of uridine, viewed along the a* direction.

distances is only 0·0064 Å, compared to the value of about 0·007 Å that would have been predicted from the formal e.s.d.'s. These latter numbers would suggest that the e.s.d.'s are approximately correct, and would ultimately lead to the conclusion that the bond distances in the two molecules are significantly different. While it is enticing to attempt to rationalize the apparent differences between the two molecules, as, for example, the effect of the larger thermal parameters shown, in general, by the atoms of molecule B, particularly since the pyrimidine ring appears to be larger in molecule A than in B, we would prefer to take a view with more perspective. Without assuming undue gravity, we conclude that the discrepancy between the dimensions of the two molecules is but another example of the surprises that can be generated by the statistics of relatively small samples.

A number of bond angles, particularly those involving exocyclic atoms in the ribose grouping, show appreciable differences in the two molecules. Most prominent of these is the C(2')–C(3')–O(3') angle, where the difference of 4·1° is highly significant. In 5-methyluridine (Hunt & Subramanian, 1969) the value of this angle is 110·7 ± 0·5°, or 6·5° smaller than in molecule B of uridine. While we presume that these variations are due to the exigencies of hydrogen bonding, we find it surprising that this one angle seems to be so especially sensitive. Distances and angles involving the hydrogen atoms are given in Table 4; here, the agreement among equivalent values is quite satisfactory.

The pyrimidine ring in molecule B is planar within experimental error (Table 5); however, it is appreciably non-planar in molecule A. The distortions in molecule A arise primarily from twists of about 2° around the N(1)–C(2) and C(5)–C(4) bonds, in opposite senses; as a result, the oxygen atoms O(2) and O(4) are displaced from the mean plane in a direction opposite from N(3). We presume that these twists result from the demands of hydrogen bonding and other intermolecular contacts.

The conformations of the two independent molecules are strikingly similar (see Fig. 1). In each case, the conformation about the glycosidic bond N(1)–C(1') is

Table 4. *Bond distances and angles involving the hydrogen atoms*

Estimated standard deviations are in the range 0·025–0·035 Å and 1·5–3·0°.

	A	B		A	B		A	B
N(3)–H(1)	0·94 Å	0·83 Å	C(2)–N(3)–H(1)	118°	115°	C(4)—N(3)–H(1)	116°	117°
C(5)–H(2)	0·96	0·93	C(4)–C(5)–H(2)	118	119	C(6)—C(5)–H(2)	122	121
C(6)–H(3)	1·00	0·94	C(5)–C(6)–H(3)	124	123	N(1)—C(6)–H(3)	114	114
C(1')–H(4)	1·00	0·98	N(1)–C(1')–H(4)	110	105	O(1')–C(1')–H(4)	111	111
			C(2')–C(1')–H(4)	110	111			
C(2')–H(5)	1·01	1·02	C(1')–C(2')–H(5)	111	109	C(3')–C(2')–H(5)	114	118
O(2')–H(6)	0·92	0·83	C(2')–O(2')–H(6)	103	106	O(2')–C(2')–H(5)	112	112
C(3')–H(7)	0·97	0·97	C(2')–C(3')–H(7)	110	108	C(4')–C(3')–H(7)	109	108
O(3')–H(8)	0·89	0·91	C(3')–O(3')–H(8)	111	108	O(3')–C(3')–H(7)	108	108
C(4')–H(9)	0·94	0·99	C(3')–C(4')–H(9)	107	111	O(1')–C(4')–C(9)	108	110
			C(5')–C(4')–H(9)	110	106			
C(5')–H(10)	1·02	1·00	C(4')–C(5')–H(10)	106	109	O(5')–C(5')–H(10)	110	107
C(5')–H(11)	0·97	0·98	C(4')–C(5')–H(11)	110	110	O(5')–C(5')–H(11)	111	108
O(5')–H(12)	0·91	0·96	C(5')–O(5')–H(12)	113	107	H(10)–C(5')–H(11)	109	109

Table 5. Deviations (Å) from the planes of the pyrimidine rings

Equations of the least-squares planes through atoms N(1)–C(6), all weighted equally, are:

Molecule A: $0.6607ax - 0.6732by + 0.2677cz = 2.098$ Å

Molecule B: $0.7054ax - 0.5246by + 0.4075cz = -0.0986$ Å.

The coefficients are direction cosines relative to the crystallographic axes:

	A	B		A	B
N(1)	0.003	−0.007	O(2)	0.073	0.015
C(2)	0.016	0.004	O(4)	0.057	0.012
N(3)	−0.027	0.000	C(1′)	0.066	0.030
C(4)	0.017	−0.002	H(1)	−0.08	−0.07
C(5)	0.002	−0.001	H(2)	0.05	0.01
C(6)	−0.011	0.006	H(3)	−0.03	−0.06

anti, the puckering of the ribose ring is C(3′) endo, and the conformation about C(4′)–C(5′) is gauche–gauche. The important torsion angles are given in Table 6. Of particular note in molecule A is the relatively close approach between atoms C(6) and O(5′), 3·112 Å; the distance H(3)···O(5′) is only 2·22 Å. These distances suggest a weak hydrogen bond that at first glance might be important in determining the molecular conformation. However, in molecule B, whose conformation is very similar to that of A, the C(6)··· O(5′) and H(3)···O(5′) distances of 3·548 and 2·62 Å are considerably too long to represent an important interaction. In 5-methyluridine (Hunt & Subramanian, 1969), which adopts a similar conformation, the distances are 3·429 and 2·51 Å.

Table 6. Torsion angles

A positive angle describes a right-handed screw. Standard deviations are about 0·3°.

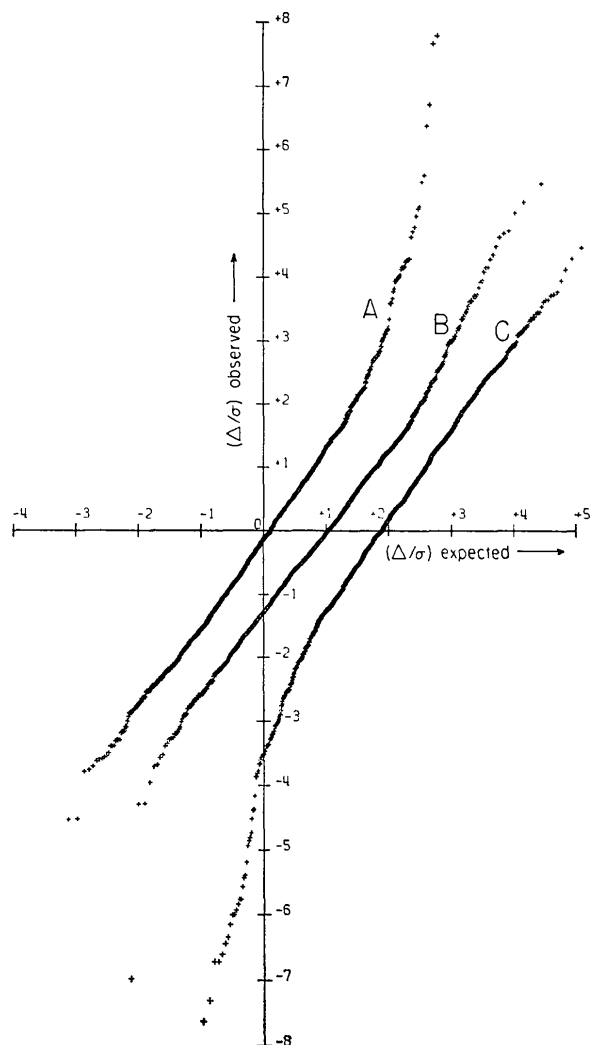|	A	B
C(6)–N(1)–C(1′)–O(1′)	18·3°	24·3°
O(1′)–C(1′)–C(2′)–C(3′)	−31·4	−27·9
C(1′)–C(2′)–C(3′)–C(4′)	39·5	40·4
C(2)′–C(3′)–C(4′)–O(1′)	−34·6	−39·5
C(3′)–C(4′)–O(1′)–C(1′)	15·3	22·8
C(4′)–O(1′)–C(1′)–C(2′)	10·5	3·4
C(3′)–C(4′)–C(5′)–O(5′)	45·9	39·6
O(1′)–C(4′)–C(5′)–O(5′)	−72·9	−77·7

Fig. 3. Normal probability plots (Abrahams & Keve, 1971) relating the individual data sets with the averaged data set. Here, Δ is the difference $(F_i^2 - F_{ave}^2)$ between a measurement from data set i and the value obtained from averaging all three data sets; σ is the standard deviation of that difference. A: Mo $K\alpha$ data collected at Pittsburgh; B: Cu $K\alpha$ data collected at Caltech; C: Cu $K\alpha$ data collected at Pittsburgh. The origins for curves B and C have been displaced to the right by 1 and 2 units.

Table 7. Hydrogen bonds D–H···A

Donor(D)	Hydrogen(H)	Acceptor(A)	in molecule at	D···A	H···A	$\angle D$–H···A
N(3) (A)	H(1) (A)	O(4) (B)	$1+x$, y, z	2·771 Å	1·84 Å	170°
O(2′) (A)	H(6) (A)	O(3′) (B)	x, $y−1$, z	2·959	2·11	153
O(3′) (A)	H(8) (A)	O(4) (A)	$2−x$, $y−\frac{1}{2}$, $1−z$	2·721	1·83	177
O(5′) (A)	H(12) (A)	O(5′) (B)	$1−x$, $y−\frac{1}{2}$, $1−z$	2·772	1·87	170
N(3) (B)	H(1) (B)	O(3′) (B)	$1−x$, $y−\frac{1}{2}$, $−z$	3·023	2·39	133
N(3) (B)	H(1) (B)	O(2′) (B)	$2−x$, $y−\frac{1}{2}$, $−z$	2·930	2·37	125
O(2′) (B)	H(6) (A)	O(2) (A)	$2−x$, $y+\frac{1}{2}$, $−z$	2·769	1·95	171
O(3′) (B)	H(8) (B)	O(2) (B)	$2−x$, $y+\frac{1}{2}$, $−z$	2·781	1·96	149
O(5′) (B)	H(12) (B)	O(3′) (A)	x, $y+1$, z	2·774	1·84	165
C(5) (B)	H(2) (B)	O(4) (A)	$x−1$, y, z	3·258	2·42	150

A drawing of the structure is shown in Fig. 2 and the details of the hydrogen bonding are given in Table 7. All available protons are involved in hydrogen bonds, although the N(3)–H(1) group of molecule B chooses to make two very weak bonds rather than one strong one – a clear case of bifurcation. The C(5)–H($2B$)···O($4A$) interaction is included in Table 7; although the distances are at the upper limit for hydrogen bonds, the array is approximately linear and there is considerable prior evidence that the C(5) and C(6) groups of pyrimidine rings can act as weak hydrogen-bond donors.

The pyrimidine rings of molecules A and B form a fairly intimate, but highly off-set, stacked pair. The dihedral angle between the two rings is 12°, and the maximum overlap involves the grouping C(2)–N(3)–C(4) of molecule A and O(4)–C(4)–C(5)–C(6) of molecule B. Within this pair, the closest contacts are C(2)···O(4), 3·191 Å; N(3)···C(4), 3·406 Å; and H(1)···C(4), 3·408 Å.

Comparison of data sets

After completion of the structure refinement, the three different data sets (two collected at Pittsburgh and one at Caltech) were compared, using the lack-of-confidence factor of 0·02 for all three. For each reflection common to at least two data sets, the weighted average values of the observed intensity amplitude F^2 and of its standard deviation were calculated. Then, for each data set, the discrepancies between the individual and average values of F^2 were calculated and compared with the values to be expected from a normal distribution about the standard deviations [see Abrahams & Keve (1971)]. The resulting plots are shown in Fig. 3. The plot for data set A, collected at Pittsburgh using molybdenum radiation, shows a large skewness at the top of the curve, while the plot of data set C, collected at Pittsburgh using copper radiation, is skewed at the lower end. Data set B, collected at Caltech using copper radiation, and used in the final refinement, is represented by a relatively straight line with a slope only slightly greater than 1·0. In general, the same reflections – often, but not always, strong low-angle ones – are responsible for the two skew regions in curves A and C; the implied errors in the measurements of these re-flections are presumably responsible for the less satisfactory refinement attained at Pittsburgh.

Conclusion

The independent molecules of uridine in this structure and the 5-methyluridine molecule in crystals of its hemihydrate (Hunt & Subramanian, 1969) have grossly different environments in terms of hydrogen bonding, base stacking, and other intermolecular contacts. Nevertheless, all three molecules have strikingly similar conformations, and at first glance, one would suspect that this conformation represents a relatively sharp and well defined minimum in the potential function for the isolated molecule. However, major differences in the geometric details of the three molecules – such as the coplanarities of the pyrimidine atoms, the C(2')–C(3')–O(3') bond angle, and the C(6)–H···O(5') interaction – suggest energy differences that intuitively are comparable with the energies associated with major conformational changes, and one infers that none of the molecules has found a true energy minimum. Once again we must face the realization that crystallization entails a delicate compromise between numerous interatomic forces, and that the presumption that the geometry of an isolated molecule can be confidently predicted from its geometry in a crystal is a very tenuous one.

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