Acta Cryst. (1973). B**29**, 61

3-Deazauridine: Crystal Structure, Conformational Parameters, and Molecular Orbital Calculations

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(*Received* 7 *August* 1972; *accepted* 31 *August* 1972)

The cytostatic compound 3-deazauridine crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell of dimensions $a=13{\cdot}394$, $b=8{\cdot}335$, $c=9{\cdot}639$ Å. On a four-circle diffractometer 998 reflexions were measured. A trial structure was obtained by direct methods and refined by least-squares procedures to $R=\sum||F_o|-|F_c||/\sum|F_o|=4{\cdot}0\%$. The tautomeric form present in the crystal is the enol, 4-hydroxy-1-(β-D-*ribo*-pentafuranosyl)-2-pyridone, which also predominates in solution. Conformational features of the nucleoside include a glycosidic bond conformation in the *anti* range, a ribose moiety in the C(2′)-*endo* envelope form and a *gauche–gauche* arrangement about the C(4′)–C(5′) bond. Pyridone units form endless chains parallel to **c** firmly linked by O(4)–H···O(2) hydrogen bonds only 2·549 Å long. Base planes make a 21° angle with the *ac* plane; stacking interactions appear insignificant. Instead, the chains are tethered at the ribose oxygens by hydrogen bonds involving H(O3′) in a bifurcated system as well as H(O2′) and H(O5′). The bifurcated hydrogen bond involves a very unusual intramolecular O(3′)–H···O(2′) and an O(3′)–H···O(4) hydrogen bond. Extended Hückel molecular orbital calculations of the electronic properties are reported.

Introduction

The amino acid sequence of a protein is encoded in the nucleotide sequence of messenger ribonucleic acid (m-RNA). A sequence of three m-RNA nucleotides, the codon, directs the incorporation of one specific amino acid into the protein to be synthesized. The association of the proper amino acid with the m-RNA codon is accomplished at the ribosome with the mediation of transfer ribonucleic acids (t-RNA). Each t-RNA carries an amino acid and contains a nucleotide triplet, the anticodon, which is complementary to the codon specifying that amino acid.

The recognition of the codon by the anticodon involves the formation of three hydrogen-bonded base pairs. Two of the base pairs, those in the 5′ and middle positions, must be of the Watson & Crick (1953) type. But the third, according to the 'wobble' theory (Crick, 1966), may be of a different type. The importance of a given proton donor or acceptor group in the formation of codon–anticodon base pairs can be investigated by incorporating chemically modified nucleobases into the codon.

3-Deazauridine, formally derived from uridine (U) by replacement of NH in the 3 position by CH_2, is such a chemically modified nucleobase. In the binding of phenylalanine specific t-RNA from yeast with UUU as codon to the ribosome, 3-deazauridine may be substituted for U in the 5′ and middle positions of the codon but not in the 'wobble' position (Gassen, Schetters & Matthaei, 1972). It was the aim of the X-ray analysis described below to obtain information on hydrogen bonding and stacking properties of 3-deazauridine and to compare them with those of U.

Furthermore, the analogue 3-deazauridine has powerful cytostatic properties (Robins, Currie, Robins & Bloch, 1969). X-ray (Schwalbe, Gassen & Saenger, 1972) and n.m.r. (Currie, Robins & Robins, 1970), evidence shows that the enol tautomer 4-hydroxy-1-(β-D-*ribo*-pentafuranosyl)-2-pyridone is the form found in the crystalline state and predominates in solution. Computerized model studies (Schwalbe, Gassen & Saenger, 1972) demonstrated a possible base pair with two hydrogen bonds between this compound and guanosine or cytidine as well as a somewhat more contorted one with adenosine. Thus a possible role as a cytidine analogue should not be overlooked. We report here the detailed crystal structure parameters as well as a quantum-mechanical evaluation of charge densities and bond overlap populations by the extended Hückel method.

Experimental

Crystals of 3-deazauridine were grown from water as colourless laths. Crystal data from X-ray photographs and diffractometer measurements are summarized in Table 1. One molecule constitutes the asymmetric unit. Intensity data were collected on a Stoe four circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation by a θ–2θ scan technique in which the scan width was $(80+30\tan\theta)$ steps of 0·01° in θ and 0·02° in 2θ, at 0·6 sec per step. Stationary background counts were taken for 20 sec before and after the scan. By this method 1017 reflexions were measured out to $\theta=62{\cdot}5°$. The data were corrected for Lorentz and polarization factors and assigned errors, σ, based on counting statistics as well as an allowance of 3% for machine instability (Stout & Jensen, 1968). Three reflexions with negative net count were thrown out, as were eight reflexions with indices $h21$ or $h22$ where machine error was suspected. The remaining 1006 reflexions were used in structure determination. During the late stages of refinement an extinction correction based on a plot of I_c/I_o *versus* I_c was applied and eight reflexions showing serious extinction effects were omitted from the data set. No correction for absorption was made. With crystal dimensions $0{\cdot}3\times0{\cdot}15\times0{\cdot}08$ mm and $\mu=10{\cdot}9$ cm^{-1} the absorption factor applied to F for straight paths would be $1{\cdot}13\pm0{\cdot}08$.

Table 1. *Crystallographic data* (*estimated errors given in parentheses*)

Space group $P2_12_12_1$ (systematic extinctions of $h00$, $0k0$, $00l$ when non-zero index odd).

$a=13{\cdot}394$ (5) Å
$b=\ 8{\cdot}335$ (3)
$c=\ 9{\cdot}639$ (4)

Ambient temperature 21 (2)°
Graphite monochromatized Cu $K\alpha$ radiation $\lambda=1{\cdot}5418$ Å
Chemical formula $C_{10}H_{13}NO_6$ (M.W. 243·22)
Measured density (cyclohexane/CH_3I) 1·491 (4) g cm^{-3}
Calculated density ($Z=4$) 1·501 g cm^{-3}
$F_{000}=512$

Structure determination and refinement

Normalized structure factors (Karle & Hauptman, 1956) were computed by the equation $E_h=(F_h^2/\langle F^2\rangle)^{1/2}$, where $\langle F^2\rangle$ is a local average over $\frac{1}{20}$ the total range of $\sin\theta$. The average values of 0·862 for E and 0·776 for (E^2-1) are close to the 0·886 and 0·736 expected (Hanic, 1966) for a non-centrosymmetric structure.

A multiple-solution procedure (Main, Germain & Woolfson, 1970) using the tangent formula (Karle & Hauptman, 1956) produced a trial structure very expeditiously from seven starting reflexions, two general and five of restricted phase. Out of 32 starting phase combinations, 2 led to different E maps (146 E's) that both revealed all 17 non-hydrogen atoms. Least-squares refinement (Busing, Martin & Levy, 1962) of coordinates as well as isotropic temperature factors in which the function $\sum 1/\sigma^2(|F_{\rm obs}|-1/K|F_{\rm calc}|)^2$ was minimized proceeded to convergence at a discrepancy index $R=\sum||F_{\rm obs}|-|F_{\rm calc}||/\sum|F_{\rm obs}|$ of 0·139. Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Refinement with anisotropic thermal parameters reduced R to 0·082, at which point all hydrogen atoms appeared in a difference electron-density synthesis at 0·28–0·60 e Å^{-3} compared with background to 0·27 e A^{-3}. Further refinement of non-hydrogen atoms with anisotropic thermal parameters followed by hydrogen atom coordinates with thermal parameters fixed at those of the attached atoms converged at $R=4{\cdot}0\%$. At this point, all parameter shifts were $\frac{1}{3}$ or less the standard deviation for hydrogens and $\frac{1}{10}$ for non-hydrogen atoms.

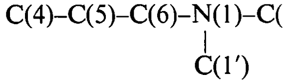
Results

Observed and calculated structure factors are presented in Table 2, atomic coordinates and thermal parameters in Table 3, and bond angles involving hydrogen atoms in Table 4. Conformationally significant least-squares planes and dihedral angles appear in Tables 5 and 6, respectively. Table 7 characterizes the hydrogen bonds. Figs. 1 and 2 are sketches of 3-deazauridine (D) showing the numbering convention with all bond distances and non-hydrogen atom bond angles. Fig. 3 is a stereoscopic view (Johnson, 1965) of the molecule, in which the ellipsoids of thermal motion follow the 50% probability contour. Fig. 4 is a projection of the crystal structure along the b axis (molecules related by $\mathbf{s}_b$, the screw axis with translation along **b**, have been omitted for clarity). Fig. 5 shows a stereo view of the structure along **c**.

Discussion

(*a*) *The* 3-*deazauracil moiety*

Inspection of the heterocycle reveals that there is a regular alternation in the C–C bond distances (Fig. 1, labelled D): 1·425 (6), 1·363 (6), 1·422 (6), and 1·361 (6) Å for C(2)–C(3), C(3)–C(4), C(4)–C(5), and C(5)–C(6) respectively. The range is not as great as that between C–C single [1·465 (5) Å], and double [1·336 (5) Å] bond lengths (Sutton, 1965) involving sp^2 hybridized carbon in conjugated dienes; consequently there must be considerable delocalization of electrons. An aromatic C–C bond would be 1·394 (5) Å long. At nitrogen the N(1)–C(2) bond is 0·03 Å longer than N(1)–C(6) despite sp^2 hybridization of both carbons, and 0·08 Å shorter than N(1)–C(1′), where the hybridization is sp^3. When one compares (Fig. 1) corresponding bonds in the following portion of the heterocycle common to 3-deazauridine (D), cytidine (C) and uridine (U) derivatives (Voet & Rich, 1970):



$$\begin{array}{c}\text{C(4)–C(5)–C(6)–}\underset{\displaystyle\text{C(1′)}}{\underset{|}{\text{N(1)}}}\text{–C(2),}\end{array}$$

one finds a maximum variation of 0·02 Å. The changes in positions 3 and 4 have more of an effect on the C(2)–O(2) bond, where the 1·255 (5) observed in D is unusually long. Several observations show that 3-deazauridine exists as the 4-hydroxy tautomeric form in the crystalline state. The C(4)–O(4) distance in D, 1·341 (5) Å, suggests a single bond, although shorter than the aromatic C–OH distance (Sutton, 1965) of 1·36 (1) Å. Further evidence for the enol form is provided by the location and refinement of hydrogen atoms H(3) and H(O4), and by the strict planarity of the heterocyclic ring (Table 5). C(3) deviates only 0·028 Å from the C(4)–C(5)–C(6)–N(1)–C(2) plane, and H(3) is only 0·13 Å out of this plane. If there were a CH_2 group at position 3, there would be no reason for C(3) to lie strictly in the plane, and its attached hydrogens should be at least 0·7 Å out of plane.

Table 2. *Observed and calculated structure factors* (× 10)

H	K	L	FOBS	FCAL
4	0	0	180	186
6	0	0	13	10
8	0	0	156	146
10	0	0	103	100
12	0	0	65	68
14	0	0	119	117
1	1	0	55	52
2	1	0	109	109
3	1	0	18	16
4	1	0	71	70
5	1	0	721	680
6	1	0	194	195
7	1	0	158	156
8	1	0	51	45
9	1	0	15	10
10	1	0	100	101
11	1	0	153	156
12	1	0	74	77
13	1	0	82	77
14	1	0	84	82
15	1	0	58	63
3	2	0	365	383
4	2	0	363	377
5	2	0	57	58
6	2	0	317	319
7	2	0	264	259
8	2	0	65	59
9	2	0	196	193
10	2	0	52	50
11	2	0	75	78
12	2	0	65	65
13	2	0	39	42
14	2	0	38	31
15	2	0	41	41
1	3	0	391	399
2	3	0	255	254
3	3	0	82	81
4	3	0	64	54
5	3	0	211	202
6	3	0	304	307
7	3	0	147	148
8	3	0	92	98
9	3	0	120	118
10	3	0	175	186
11	3	0	83	88
12	3	0	58	59
13	3	0	17	15
14	3	0	83	81
0	4	0	126	113
1	4	0	285	279
2	4	0	222	221
3	4	0	158	154
4	4	0	78	78
5	4	0	16	20
6	4	0	56	58
7	4	0	156	156
8	4	0	142	139
9	4	0	101	109
10	4	0	124	122
11	4	0	98	97
12	4	0	45	50
13	4	0	48	44
14	4	0	45	40
1	5	0	149	140
2	5	0	303	315
3	5	0	45	46
4	5	0	260	258
5	5	0	9	4
6	5	0	30	30
7	5	0	93	97
8	5	0	87	84
9	5	0	44	42
10	5	0	37	33
11	5	0	27	27
12	5	0	25	24
13	5	0	47	47
0	6	0	147	137
1	6	0	77	78
2	6	0	155	155
3	6	0	12	8
4	6	0	12	17
5	6	0	141	143
6	6	0	100	106
7	6	0	96	100
8	6	0	76	75
9	6	0	36	41
10	6	0	15	12
11	6	0	59	56
12	6	0	45	46
1	7	0	7	13
2	7	0	8	1
3	7	0	44	49
4	7	0	55	60
5	7	0	115	108
6	7	0	32	31
7	7	0	28	32
8	7	0	47	48
9	7	0	44	38
10	7	0	16	14
0	8	0	58	56
1	8	0	12	19
2	8	0	18	3
3	8	0	10	11
4	8	0	73	67
5	8	0	72	66
6	8	0	70	74
7	8	0	47	45
8	8	0	15	12
1	9	0	21	23
2	9	0	5	8
3	9	0	9	10
4	9	0	12	13
5	9	0	48	43
1	0	1	20	6
3	0	1	112	119
4	0	1	92	88
5	0	1	412	408
6	0	1	532	513
7	0	1	257	261
8	0	1	183	182
9	0	1	164	166
10	0	1	136	142
11	0	1	55	55
12	0	1	72	72
14	0	1	169	172
15	0	1	48	52
0	1	1	355	389
1	1	1	366	416
3	1	1	130	138
4	1	1	489	500
5	1	1	238	240
6	1	1	191	193
7	1	1	45	46
8	1	1	161	162
9	1	1	54	51
10	1	1	166	168
11	1	1	127	132
12	1	1	25	18
13	1	1	52	50
14	1	1	40	39
15	1	1	29	23
0	2	1	134	132
2	2	1	287	292
3	2	1	152	157
4	2	1	298	307
5	2	1	120	92
6	2	1	348	331
7	2	1	163	152
14	2	1	37	31
15	2	1	60	51
0	3	1	714	684
1	3	1	445	463
2	3	1	207	210
3	3	1	273	272
4	3	1	416	414
5	3	1	221	228
6	3	1	139	134
7	3	1	96	98
8	3	1	165	168
9	3	1	43	39
10	3	1	58	60
11	3	1	120	123
12	3	1	52	48
13	3	1	48	46
14	3	1	34	32
0	4	1	36	34
1	4	1	92	89
2	4	1	164	168
3	4	1	274	282
4	4	1	93	89
5	4	1	358	352
6	4	1	93	92
7	4	1	44	39
8	4	1	75	76
9	4	1	40	43
10	4	1	83	82
11	4	1	33	35
12	4	1	17	15
13	4	1	40	37
0	5	1	6	9
1	5	1	250	259
2	5	1	176	175
3	5	1	99	103
4	5	1	268	274
5	5	1	20	23
6	5	1	120	124
7	5	1	123	130
8	5	1	141	145
9	5	1	168	173
10	5	1	106	107
11	5	1	36	33
12	5	1	7	6
13	5	1	24	25
0	6	1	35	36
1	6	1	65	69
2	6	1	47	47
3	6	1	159	166
4	6	1	103	107
5	6	1	52	54
6	6	1	146	152
7	6	1	75	78
8	6	1	77	75
9	6	1	68	72
10	6	1	59	61
11	6	1	74	71
0	7	1	111	112
1	7	1	49	52
2	7	1	23	31
3	7	1	118	130
4	7	1	124	132
5	7	1	110	107
6	7	1	135	132
7	7	1	67	64
8	7	1	129	132
9	7	1	58	57
10	7	1	21	21
0	8	1	11	1
1	8	1	45	43
2	8	1	25	34
3	8	1	91	96
4	8	1	52	46
5	8	1	39	41
6	8	1	45	42
7	8	1	67	68
8	8	1	59	55
0	9	1	18	13
1	9	1	75	73
2	9	1	12	10
3	9	1	40	41
4	9	1	61	63
5	9	1	64	62
1	0	2	301	328
2	0	2	409	439
3	0	2	47	43
4	0	2	158	154
5	0	2	430	440
6	0	2	206	192
7	0	2	172	111
8	0	2	239	254
9	0	2	160	163
10	0	2	127	133
11	0	2	146	148
12	0	2	98	101
13	0	2	46	46
14	0	2	14	0
15	0	2	9	6
0	1	2	60	56
1	1	2	439	476
2	1	2	283	301
3	1	2	374	332
4	1	2	195	202
5	1	2	60	63
6	1	2	178	170
7	1	2	203	199
8	1	2	142	147
9	1	2	33	27
10	1	2	110	115
11	1	2	182	190
12	1	2	219	233
13	1	2	76	80
14	1	2	28	27
15	1	2	60	59
0	2	2	268	248
1	2	2	499	529
2	2	2	122	94
3	2	2	114	119
4	2	2	192	192
6	2	2	96	95
7	2	2	175	187
8	2	2	118	113
9	2	2	144	145
10	2	2	213	215
11	2	2	102	100
12	2	2	69	69
13	2	2	80	80
14	2	2	38	38
0	3	2	43	36
1	3	2	333	335
2	3	2	432	449
3	3	2	406	423
4	3	2	409	400
5	3	2	128	125
6	3	2	89	86
7	3	2	147	143
8	3	2	95	95
9	3	2	150	157
10	3	2	190	196
11	3	2	206	219
12	3	2	85	87
13	3	2	59	63
14	3	2	16	16
0	4	2	204	202
1	4	2	142	144
2	4	2	250	261
3	4	2	18	19
4	4	2	210	214
5	4	2	79	77
6	4	2	66	70
7	4	2	170	185
8	4	2	49	47
9	4	2	147	148
10	4	2	111	113
11	4	2	44	47
12	4	2	62	62
13	4	2	18	17
0	5	2	13	9
1	5	2	239	236
2	5	2	58	61
3	5	2	194	200
4	5	2	108	110
5	5	2	31	27
6	5	2	115	115
7	5	2	59	59
8	5	2	115	114
9	5	2	145	153
10	5	2	75	78
11	5	2	50	48
12	5	2	34	33
0	6	2	68	64
1	6	2	52	56
2	6	2	60	59
3	6	2	244	250
4	6	2	182	190
5	6	2	126	125
6	6	2	95	95
7	6	2	59	61
8	6	2	131	136
9	6	2	78	77
10	6	2	71	66
11	6	2	15	16
0	7	2	92	82
1	7	2	15	13
2	7	2	71	77
3	7	2	60	64
4	7	2	48	50
5	7	2	87	90
6	7	2	57	55
7	7	2	45	41
8	7	2	105	103
9	7	2	38	35
10	7	2	64	62
0	8	2	141	141
1	8	2	45	47
2	8	2	40	42
3	8	2	96	99
4	8	2	38	38
5	8	2	120	117
6	8	2	47	45
7	8	2	72	66
8	8	2	57	56
0	9	2	3	0
1	9	2	27	29
2	9	2	21	23
3	9	2	28	25
4	9	2	42	43
1	0	3	104	98
2	0	3	388	397
3	0	3	99	98
4	0	3	691	626
5	0	3	72	69
6	0	3	135	129
7	0	3	235	237
8	0	3	11	10
9	0	3	120	126
10	0	3	100	106
11	0	3	62	63
12	0	3	140	149
13	0	3	33	33
14	0	3	135	132
0	1	3	154	155
1	1	3	339	327
2	1	3	245	249
3	1	3	297	294
4	1	3	385	377
5	1	3	174	169
6	1	3	174	161
7	1	3	190	193
8	1	3	141	146
9	1	3	83	89
10	1	3	20	21
11	1	3	253	253
12	1	3	169	165
13	1	3	143	143
14	1	3	42	44
0	2	3	13	8
1	2	3	228	232
2	2	3	202	199
3	2	3	244	244
4	2	3	262	230
5	2	3	104	103
6	2	3	297	290
7	2	3	168	167
8	2	3	56	49
9	2	3	170	169
10	2	3	116	123
11	2	3	46	45
12	2	3	65	61
13	2	3	148	151
14	2	3	52	48
0	3	3	38	38
1	3	3	61	54
2	3	3	189	189
3	3	3	80	77
4	3	3	298	280
5	3	3	233	226
6	3	3	78	66
7	3	3	93	93
8	3	3	117	123
9	3	3	75	81
10	3	3	44	43
11	3	3	149	151
12	3	3	96	94
13	3	3	49	47
14	3	3	72	66
0	4	3	157	162
1	4	3	143	146
2	4	3	355	342
3	4	3	131	129
4	4	3	185	179
5	4	3	84	80
6	4	3	34	32
7	4	3	103	98
8	4	3	89	95
9	4	3	112	116
10	4	3	56	57
11	4	3	52	54
12	4	3	77	76
13	4	3	105	102
0	5	3	91	91
1	5	3	8	10
2	5	3	103	108
3	5	3	45	41
4	5	3	57	51
5	5	3	61	59
6	5	3	40	46
7	5	3	103	103
8	5	3	99	102
9	5	3	70	72
10	5	3	25	27
11	5	3	20	15
12	5	3	56	56
0	6	3	31	34
1	6	3	45	43
2	6	3	132	131
3	6	3	100	99
4	6	3	101	101
5	6	3	57	61
6	6	3	97	95
7	6	3	10	12
8	6	3	21	21
9	6	3	99	98
10	6	3	54	50
11	6	3	59	60
0	7	3	10	6
1	7	3	75	77
2	7	3	51	51
3	7	3	46	47
4	7	3	88	90
5	7	3	72	72
6	7	3	57	54
7	7	3	35	34
8	7	3	41	38
9	7	3	27	27
0	8	3	8	13
1	8	3	72	69
2	8	3	33	33
3	8	3	61	59
4	8	3	45	47
5	8	3	30	26
6	8	3	37	35
7	8	3	37	34
0	9	3	33	35
1	9	3	16	16
2	9	3	20	14
3	9	3	44	42
0	0	4	89	85
1	0	4	315	300
2	0	4	193	189
3	0	4	158	157
4	0	4	27	32
5	0	4	95	89
6	0	4	118	118
7	0	4	408	396
8	0	4	154	151
9	0	4	25	30
10	0	4	76	83
11	0	4	56	58
12	0	4	75	75
13	0	4	10	9
14	0	4	17	2
0	1	4	47	48
1	1	4	149	153
2	1	4	448	417
3	1	4	330	323
4	1	4	281	275
5	1	4	379	350
6	1	4	271	259
7	1	4	58	57
8	1	4	57	62
9	1	4	113	115
10	1	4	116	119
11	1	4	100	102
12	1	4	41	38
13	1	4	94	90
14	1	4	35	35
0	2	4	161	165
1	2	4	397	378
2	2	4	245	246
3	2	4	231	223
4	2	4	153	156
5	2	4	79	67
6	2	4	126	125
8	2	4	200	201
9	2	4	67	67
10	2	4	81	84
11	2	4	110	117
12	2	4	73	72
13	2	4	65	62
14	2	4	67	69
0	3	4	101	103
1	3	4	132	125
2	3	4	147	152
3	3	4	184	195
4	3	4	80	74
5	3	4	128	123
6	3	4	201	204
7	3	4	132	131
8	3	4	212	212
9	3	4	93	97
10	3	4	106	111
11	3	4	49	48
12	3	4	99	101
13	3	4	47	44
0	4	4	76	77
1	4	4	109	113
2	4	4	54	57
3	4	4	58	53
4	4	4	97	104
5	4	4	144	141
6	4	4	42	44
7	4	4	124	126
8	4	4	65	70
9	4	4	96	100
10	4	4	136	143
11	4	4	19	21
12	4	4	117	114
0	5	4	42	44
1	5	4	71	68
2	5	4	52	54
3	5	4	102	94
4	5	4	119	121
5	5	4	87	83
6	5	4	134	134
7	5	4	140	137
8	5	4	82	83
9	5	4	44	48
10	5	4	29	32
11	5	4	25	23
0	6	4	22	25
1	6	4	108	109
2	6	4	38	41
3	6	4	68	73
4	6	4	29	31
5	6	4	101	102
6	6	4	62	61
7	6	4	61	59
8	6	4	62	62
9	6	4	55	56
10	6	4	30	29
0	7	4	70	74
1	7	4	44	47
2	7	4	99	94
3	7	4	11	6
4	7	4	64	62
5	7	4	19	20
6	7	4	59	54
7	7	4	44	45
8	7	4	22	21
0	8	4	46	46
1	8	4	43	43
2	8	4	43	44
3	8	4	32	29
4	8	4	51	48
5	8	4	32	29
6	8	4	3	9
1	0	5	132	124
2	0	5	213	199
3	0	5	117	109
4	0	5	27	28
5	0	5	77	78
6	0	5	18	21
7	0	5	291	296
8	0	5	69	64
9	0	5	126	125
10	0	5	42	41
11	0	5	36	36
12	0	5	80	70
13	0	5	26	27
0	1	5	68	71
1	1	5	183	181
2	1	5	271	254
3	1	5	184	186
4	1	5	165	153
5	1	5	203	200
6	1	5	58	61
7	1	5	68	67
8	1	5	160	160
9	1	5	290	293
10	1	5	227	228
11	1	5	162	156
12	1	5	86	79
13	1	5	46	47
0	2	5	205	214
1	2	5	226	219
2	2	5	79	65
3	2	5	125	115
4	2	5	40	37
5	2	5	187	187
6	2	5	154	152
8	2	5	59	59
10	2	5	15	12
11	2	5	113	108
12	2	5	91	85
13	2	5	28	23
0	3	5	61	54
1	3	5	158	154
2	3	5	74	61
3	3	5	379	352
4	3	5	84	80
5	3	5	43	39
6	3	5	111	109
7	3	5	170	174
8	3	5	126	125
9	3	5	98	94
10	3	5	137	134
11	3	5	70	67
12	3	5	38	33
0	4	5	233	227
1	4	5	93	92
2	4	5	157	157
3	4	5	109	111
4	4	5	75	72
5	4	5	25	21
6	4	5	79	80
7	4	5	124	126
8	4	5	103	105
9	4	5	131	130
10	4	5	70	65
11	4	5	40	33
12	4	5	18	14
0	5	5	154	150
1	5	5	24	19
2	5	5	82	85
3	5	5	40	36
4	5	5	96	98
5	5	5	114	112
6	5	5	54	56
7	5	5	91	94
8	5	5	81	75
9	5	5	32	26
10	5	5	60	57
11	5	5	66	60
0	6	5	107	107
1	6	5	41	39
2	6	5	70	73
3	6	5	110	110
4	6	5	76	77
5	6	5	20	18
6	6	5	23	21
7	6	5	23	20
8	6	5	77	73
9	6	5	39	34
0	7	5	55	55
1	7	5	46	45
2	7	5	19	14
3	7	5	59	57
4	7	5	32	30
5	7	5	25	23
6	7	5	37	37
7	7	5	14	12
0	8	5	23	20
1	8	5	51	51
2	8	5	16	15
3	8	5	71	67
4	8	5	40	39
0	0	6	186	182
1	0	6	52	52
2	0	6	174	184
3	0	6	95	99
4	0	6	128	129
5	0	6	91	92
6	0	6	99	101
7	0	6	202	210
8	0	6	73	71
9	0	6	101	113
10	0	6	10	3
11	0	6	71	65
12	0	6	40	37
0	1	6	143	143
1	1	6	202	206
2	1	6	44	44
3	1	6	112	121
4	1	6	97	93
5	1	6	67	69
6	1	6	134	134
7	1	6	89	87
8	1	6	101	104
9	1	6	206	215
10	1	6	54	50
11	1	6	61	62
12	1	6	33	32
0	2	6	138	134
1	2	6	19	19
2	2	6	132	138
3	2	6	227	235
4	2	6	77	72
5	2	6	45	53
6	2	6	245	259
7	2	6	211	214
8	2	6	143	149
9	2	6	48	44
10	2	6	44	44
11	2	6	50	47
12	2	6	57	49
0	3	6	176	127
1	3	6	93	88
2	3	6	31	32
3	3	6	39	40
4	3	6	163	169
5	3	6	147	146
7	3	6	82	83
8	3	6	103	109
9	3	6	84	86
10	3	6	31	29
11	3	6	50	50
12	3	6	42	40
0	4	6	77	80
1	4	6	95	99
2	4	6	61	63
3	4	6	56	50
4	4	6	30	28
5	4	6	248	261
6	4	6	111	117
7	4	6	87	89
8	4	6	110	109
9	4	6	59	59
10	4	6	40	39
11	4	6	54	52
0	5	6	143	147
1	5	6	65	65
2	5	6	184	194
3	5	6	83	89
4	5	6	56	60
5	5	6	149	154
6	5	6	36	32
7	5	6	81	84
8	5	6	17	17
9	5	6	21	19
10	5	6	48	48
0	6	6	21	12
1	6	6	93	92
2	6	6	106	105
3	6	6	14	11
4	6	6	63	64
5	6	6	104	113
6	6	6	26	25
7	6	6	80	81
8	6	6	55	56
0	7	6	22	24
1	7	6	118	119
2	7	6	75	77
3	7	6	30	33
4	7	6	81	83
5	7	6	37	36
6	7	6	38	42
0	8	6	20	15
1	8	6	62	58
1	0	7	258	251
2	0	7	63	61
3	0	7	162	160
4	0	7	107	113
5	0	7	130	134
6	0	7	41	42
7	0	7	11	10
8	0	7	111	121
9	0	7	121	126
10	0	7	121	121
11	0	7	35	36
0	1	7	10	15
1	1	7	162	167
2	1	7	23	17
3	1	7	58	59
4	1	7	74	77
5	1	7	128	126
6	1	7	81	82
7	1	7	46	48
8	1	7	126	124
9	1	7	37	37
10	1	7	79	76
11	1	7	33	33
0	2	7	280	283
1	2	7	152	148
2	2	7	178	180
3	2	7	158	160
4	2	7	87	92
5	2	7	44	40
6	2	7	107	111
7	2	7	72	77
8	2	7	93	92
9	2	7	67	59
10	2	7	57	56
11	2	7	60	62
0	3	7	78	78
1	3	7	232	236
2	3	7	8	6
3	3	7	134	136
4	3	7	40	39
5	3	7	111	114
6	3	7	109	113
7	3	7	89	89
8	3	7	27	33
9	3	7	60	55
10	3	7	11	12
0	4	7	141	143
1	4	7	207	207
2	4	7	36	38
3	4	7	98	97
4	4	7	83	84
5	4	7	31	31
6	4	7	47	46
7	4	7	66	62
8	4	7	93	94
9	4	7	47	40
10	4	7	29	26
0	5	7	195	195
1	5	7	29	29
2	5	7	87	85
3	5	7	98	98
4	5	7	91	89
5	5	7	17	15
6	5	7	150	150
7	5	7	90	93
8	5	7	51	46
0	6	7	88	86
1	6	7	116	116
2	6	7	23	17
3	6	7	51	50
4	6	7	61	57
5	6	7	22	21
6	6	7	29	26
7	6	7	46	47
0	7	7	17	19
1	7	7	36	34
2	7	7	61	61
3	7	7	44	42
4	7	7	56	53
0	0	8	32	32
1	0	8	117	113
2	0	8	226	231
3	0	8	150	150
4	0	8	70	76
5	0	8	51	53
6	0	8	43	46
7	0	8	78	77
8	0	8	46	46
9	0	8	61	55
10	0	8	35	37
0	1	8	92	88
1	1	8	90	89
2	1	8	130	137
3	1	8	80	82
4	1	8	235	232
5	1	8	178	185
6	1	8	89	88
7	1	8	48	45
8	1	8	42	46
9	1	8	76	73
10	1	8	32	37
0	2	8	29	27
1	2	8	127	131
2	2	8	161	165
3	2	8	116	114
4	2	8	56	52
5	2	8	154	168
6	2	8	33	35
7	2	8	95	98
8	2	8	96	98
9	2	8	73	71
10	2	8	65	72
0	3	8	30	26
1	3	8	140	147
2	3	8	39	43
3	3	8	120	124
4	3	8	95	94
5	3	8	125	131
6	3	8	70	75
7	3	8	24	21
8	3	8	29	25
9	3	8	20	23
0	4	8	58	61
1	4	8	90	93
2	4	8	96	97
3	4	8	73	72
4	4	8	68	66
5	4	8	99	105
6	4	8	94	97
7	4	8	21	22
8	4	8	35	37
0	5	8	75	78
1	5	8	56	59
2	5	8	24	24
3	5	8	54	54
4	5	8	97	100
5	5	8	13	11
6	5	8	89	85
7	5	8	25	23
0	6	8	37	40
1	6	8	37	38
2	6	8	26	25
3	6	8	42	40
4	6	8	19	21
1	0	9	62	60
2	0	9	115	119
3	0	9	185	192
4	0	9	40	45
5	0	9	58	62
6	0	9	15	17
7	0	9	33	9
8	0	9	27	28
9	0	9	18	16
0	1	9	15	18
1	1	9	92	95
2	1	9	120	122
3	1	9	154	150
4	1	9	27	27
5	1	9	65	67
6	1	9	62	64
7	1	9	30	26
8	1	9	31	30
0	2	9	116	117
1	2	9	60	63
2	2	9	199	192
3	2	9	83	77
4	2	9	116	114
5	2	9	38	32
6	2	9	23	21
7	2	9	75	73
8	2	9	50	50
0	3	9	27	25
1	3	9	44	46
2	3	9	43	42
3	3	9	76	79
4	3	9	86	87
5	3	9	65	66
6	3	9	97	98
7	3	9	57	58
0	4	9	64	67
1	4	9	76	81
2	4	9	79	80
3	4	9	60	58
4	4	9	61	58
5	4	9	40	39
6	4	9	74	67
0	5	9	19	16
1	5	9	28	27
2	5	9	58	53
3	5	9	20	20
4	5	9	56	50
0	0	10	27	28
1	0	10	14	12
2	0	10	64	60
3	0	10	7	2
4	0	10	70	68
5	0	10	26	27
0	1	10	19	18
1	1	10	62	59
2	1	10	66	61
3	1	10	102	98
4	1	10	55	50
5	1	10	17	14
6	1	10	45	43
0	2	10	72	73
1	2	10	41	40
2	2	10	50	49
3	2	10	67	66
4	2	10	35	35
5	2	10	74	73
0	3	10	114	106
1	3	10	58	57
2	3	10	14	18
3	3	10	41	36
4	3	10	37	34
0	4	10	15	11
1	4	10	21	21
0	0	11	8	0
1	0	11	71	69
0	1	11	25	25
1	1	11	17	16

Table 3. *Fractional atomic coordinates and anisotropic thermal parameters in the form* $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Estimated standard deviations are in parentheses

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	0·0367 (2)	0·4422 (3)	0·1321 (2)	28 (1)	126 (4)	62 (2)	4 (2)	−0 (2)	−2 (3)
C(2)	0·1338 (2)	0·4893 (4)	0·1616 (3)	32 (1)	141 (5)	73 (3)	−7 (2)	8 (2)	−6 (3)
O(2)	0·1862 (2)	0·5465 (4)	0·0657 (2)	39 (1)	318 (7)	80 (3)	−37 (3)	3 (2)	18 (3)
C(3)	0·1658 (2)	0·4713 (4)	0·3017 (3)	28 (1)	145 (5)	78 (3)	−13 (2)	−1 (2)	−20 (4)
C(4)	0·1022 (2)	0·4172 (4)	0·4018 (3)	34 (1)	105 (4)	71 (3)	−0 (2)	−2 (2)	−6 (3)
O(4)	0·1270 (2)	0·4065 (3)	0·5362 (2)	36 (1)	170 (4)	65 (2)	−13 (2)	−9 (1)	−2 (3)
C(5)	0·0030 (2)	0·3720 (4)	0·3666 (3)	35 (2)	146 (5)	71 (3)	−7 (2)	4 (2)	3 (3)
C(6)	−0·0260 (2)	0·3856 (4)	0·2318 (3)	30 (2)	133 (5)	76 (3)	−7 (2)	0 (2)	1 (3)
C(1′)	−0·0011 (2)	0·4572 (4)	−0·0102 (3)	29 (1)	117 (4)	67 (3)	−3 (2)	−0 (2)	9 (3)
O(1′)	−0·0901 (2)	0·5456 (2)	−0·0073 (2)	48 (1)	111 (3)	99 (3)	17 (2)	−11 (2)	−9 (2)
C(2′)	−0·0273 (2)	0·2974 (4)	−0·0777 (3)	34 (2)	115 (4)	69 (3)	9 (2)	2 (2)	−2 (3)
O(2′)	0·0602 (2)	0·2305 (3)	−0·1360 (2)	40 (1)	181 (4)	90 (2)	26 (2)	−3 (2)	−30 (3)
C(3′)	−0·1034 (2)	0·3502 (4)	−0·1849 (3)	34 (1)	132 (5)	67 (3)	−5 (2)	−0 (2)	8 (3)
O(3′)	−0·0543 (2)	0·4116 (3)	−0·3049 (2)	42 (1)	206 (4)	67 (2)	9 (2)	3 (1)	23 (3)
C(4′)	−0·1583 (2)	0·4867 (4)	−0·1119 (3)	33 (2)	146 (5)	80 (3)	10 (2)	1 (2)	29 (4)
C(5′)	−0·2556 (3)	0·4402 (5)	−0·0457 (4)	40 (2)	193 (6)	117 (4)	31 (3)	15 (2)	31 (5)
O(5′)	−0·2377 (2)	0·3097 (4)	0·0473 (3)	47 (1)	227 (5)	159 (4)	−2 (2)	20 (2)	81 (4)
H(3)	0·233 (3)	0·491 (5)	0·321 (4)	28	145	78	−13	−1	−20
H(O4)	0·188 (3)	0·428 (5)	0·558 (4)	36	170	65	−13	−9	−2
H(5)	−0·042 (3)	0·338 (5)	0·437 (4)	35	146	71	−7	4	3
H(6)	−0·095 (3)	0·358 (5)	0·198 (4)	30	133	76	−7	0	1
H(1′)	0·050 (3)	0·509 (5)	−0·063 (4)	29	117	67	−3	−0	9
H(2′)	−0·060 (3)	0·216 (4)	−0·017 (4)	34	115	69	9	2	−2
H(O2′)	0·042 (3)	0·139 (5)	−0·155 (4)	40	181	90	26	−3	−30
H(3′)	−0·154 (3)	0·271 (4)	−0·206 (4)	34	132	67	−5	−0	8
H(O3′)	−0·001 (3)	0·354 (5)	−0·301 (4)	42	206	67	9	3	23
H(4′)	−0·169 (3)	0·574 (5)	−0·187 (4)	33	146	80	10	1	29
H($5'_1$)	−0·282 (3)	0·542 (6)	0·006 (4)	40	193	117	21	15	31
H($5'_2$)	−0·304 (3)	0·417 (6)	−0·120 (5)	40	193	117	21	15	31
H(O5′)	−0·301 (3)	0·274 (6)	0·061 (5)	47	227	159	−2	20	81

Table 4. *Bond angles involving hydrogen atoms*

H(3)—C(3)-C(2)	117°
H(3)—C(3)-C(4)	121
H(O4)-O(4)-C(4)	117
H(5)—C(5)-C(4)	120
H(5)—C(5)-C(6)	122
H(6)—C(6)-C(5)	124
H(6)—C(6)-N(1)	114
H(1′)—C(1′)-N(1)	107
H(1′)—C(1′)-O(1′)	112
H(1′)—C(1′)-C(2′)	110
H(2′)—C(2′)-C(1′)	116
H(2′)—C(2′)-O(2′)	109
H(2′)—C(2′)-C(3′)	108
H(O2′)-O(2′)-C(2′)	102
H(3′)—C(3′)-C(2′)	115
H(3′)—C(3′)-C(4′)	106
H(O3′)-O(3′)-C(3′)	98
H(4′)—C(4′)-C(3′)	105
H(4′)—C(4′)-O(1′)	109
H(4′)—C(4′)-C(5′)	111
H($5'_1$)—C(5′)-C(4′)	107
H($5'_2$)—C(5′)-C(4′)	108
H($5'_1$)—C(5′)-O(5′)	112
H($5'_2$)—C(5′)-O(5′)	114
H($5'_1$)—C(5′)-H($5'_2$)	107
H(O5′)-O(5′)-C(5′)	101

Table 5. *Least-squares planes through heterocycles and riboses*

The plane equations are of the form $lX+mY+nZ+p=0$ where X, Y, Z are along **a**, **b** and **c**. Atoms which define the planes are marked by *.

Moiety	Plane coefficients	Atom	Deviation from plane (Å)
Heterocycle	$l=-0{\cdot}3165$	N(1)*	−0·002
	$m=0{\cdot}9312$	C(2)*	0·003
	$n=0{\cdot}1809$	O(2)	0·058
	$p=-3{\cdot}5093$	C(3)	−0·028
		C(4)*	−0·004
		O(4)	0·042
		C(5)*	0·005
		C(6)*	−0·002
		C(1′)	0·026
		C(2′)	−1·232
		H(3)	−0·13
		H(O4)	−0·01
		H(5)	0·06
		H(6)	0·02
Ribose	$l=0{\cdot}3823$	C(1′)*	−0·002
	$m=0{\cdot}6497$	C(2′)	−0·573
	$n=-0{\cdot}6571$	C(3′)*	0·002
	$p=-2{\cdot}5366$	C(4′)*	−0·003
		O(1′)*	0·003
		O(2′)	−0·119
		O(3′)	1·345
		C(5′)	−1·172
		O(5′)	−2·376

(*b*) *Ribose*

The ribose conformation is a prime example of the C(2′)-*endo* envelope form. No bond distance varies more than 0·017 Å from the average over three other C(2′)-*endo* nucleosides (Saenger & Eckstein, 1970). The O(1′)–C(4′) bond is longer than the O(1′)–C(1′), as usual. Bond angles (Fig. 2) differ from average values by no more than 1·0° except for the following angles,

Table 6. *Endocyclic and exocyclic dihedral angles within the ribose unit*

C(6)–N(1)–C(1′)–C(2′)	−65·3°
C(6)–N(1)–C(1′)–O(1′)	+52·3
C(2)–N(1)–C(1′)–C(2′)	+116·3
C(2)–N(1)–C(1′)–O(1′)	−126·2
N(1)–C(1′)–C(2′)–O(2′)	−84·7
N(1)–C(1′)–C(2′)–C(3′)	+155·3
O(1′)–C(1′)–C(2′)–O(2′)	+156·1
O(1′)–C(1′)–C(2′)–C(3′)	+36·1
C(1′)–C(2′)–C(3′)–C(4′)	−35·2
O(2′)–C(2′)–C(3′)–O(3′)	−35·2
C(1′)–C(2′)–C(3′)–O(3′)	+81·2
O(2′)–C(2′)–C(3′)–C(4′)	−151·7
C(2′)–C(3′)–C(4′)–O(1′)	+23·2
C(2′)–C(3′)–C(4′)–C(5′)	−98·0
O(3′)–C(3′)–C(4′)–C(5′)	+144·7
O(3′)–C(3′)–C(4′)–O(1′)	−94·1
O(1′)–C(4′)–C(5′)–O(5′)	−63·9
C(3′)–C(4′)–C(5′)–O(5′)	+55·1
C(3′)–C(4′)–O(1′)–C(1′)	+0·5
C(5′)–C(4′)–O(1′)–C(1′)	+124·0
C(4′)–O(1′)–C(1′)–C(2′)	−22·6
C(4′)–O(1′)–C(1′)–N(1)	−145·2

which may well be influenced by the tug on hydrogen-bonded oxygens: C(1′)–C(2′)–O(2′), 108·9° (3) in D *versus* an average 112·1°; C(2′)–C(3′)–C(4′), 103·1° (3) *vs.* 101·1°; C(2′)–C(3′)–O(3′), 110·3° (3) *vs.* 108·3°; and C(4′)–C(5′)–O(5′), 108·5° (3) *vs.* 112·7°. One (least-squares) plane passes within 0·003 Å of atoms C(1′), O(1′), C(4′), and C(3′) but misses C(2′) by 0·57 Å. The dihedral angle O(2′)–C(2′)–C(3′)–O(3′) is −35·2°. Atom O(5′) is located 'above' the ribose ring, as indicated by the dihedral angles O(5′)–C(5′)–C(4′)–O(1′) of −63·9° and O(5′)–C(5′)–C(4′)–C(3′) of 55·1°. The relation of ribose to base is specified by the dihedral angle C(2′)–C(1′)–N(1)–C(6), which is −65·3°. This value falls comfortably within the *anti* range (Saenger & Scheit, 1970), the usual one for pyrimidine nucleosides.

(*c*) *Packing arrangement*

The segregation of hydrophobic and hydrophilic zones that is so frequently found in nucleoside crystals (Saenger & Suck, 1972) also occurs in 3-deazauridine but in an unusual manner. Whereas the hydrophobic zones are usually pillars of stacked bases, here the hydrophobic structural elements are undulating endless chains of bases produced by the action of $\mathbf{s}_c$, the twofold screw axis with translation along **c** (Fig. 4). Bases in the chain are linked by a short (2·549 Å) and presumably very strong hydrogen bond between the 4-hydroxyl group and the 2-keto group of the screw-related neighbour molecule. The geometry of this hydrogen bond can be further described by the following distances: O(4)–H(O4), 0·94 Å; H(O4)–O(2$\mathbf{s}_c$), 1·70 Å; and angles: H(O4)–O(4)–O(2$\mathbf{s}_c$), 4°; C(4)–O(4)–O(2$\mathbf{s}_c$), 109·9°. This arrangement, with H(O4) almost directly on the O(4)···O(2$\mathbf{s}_c$) line and the bond angle at O(4) just a little greater than tetrahedral should be energetically favorable. Individual base planes in the hydrophobic bands, shaded in Fig. 4 to show their orientation, make 21° angles with the *ac* plane. Through the action of the twofold screw axis with translation along **b** an overlap of bases is produced (omitted from Fig. 4 for clarity), but at an angle of 42° which precludes the typical stacking interactions. These two bases form a pair of hydrophobic jaws that grasp the hydrophobic C(5′) methylene group from a neighbouring ribose, but not the hydrophilic O(5′). Thus continuity of the hydrophobic region along the **b** direction is preserved. Most nucleoside crystals contain parallel-stacked bases; 5,6-dihydrouridine (Suck, Saenger & Zechmeister, 1972), does not because the planar aromatic system has been broken up, and 5′-methylammonium-5′-deoxyadenosine iodide monohydrate (Saenger, 1971) does not presumably because of interaction between adenine heterocycles and iodide ions. In the present case hydrogen bonding is optimized, hydrophobic interaction is preserved, but polarization interactions are sacrificed.

The hydrophilic groups form an intricate network of hydrogen bonds (Table 7) involving every hydroxyl group: O(2′)–H(O2′)···O(3′$\mathbf{s}_b$), O(5′)–H(O5′)··· O(2′$\mathbf{s}_a$), and an unusual bifurcated system in which H(O3′) is in the neighborhood both of O(2′) in the same molecule and of O(4) in the molecule in the next unit cell along **c**. The intramolecular O(3′)–H···O(2′) hydrogen bond is most unusual and, to our knowledge, has not been observed in nucleoside crystal structures previously.

Molecular orbital calculations

To investigate the electronic properties of 3-deazauridine, extended Hückel (Hoffman, 1963) calculations were carried out. Although it is well known that the charge separations obtained by this method are exaggerated and the total overlap populations depend significantly on the parametrization, comparisons among closely related molecules are reliable. Good comparison standards are available in uridine and cytidine (Jordan & Pullman, 1968, abbreviated JP)

Table 7. *Distances and angles that characterize the hydrogen bonds*

Donor (*D*)	Acceptor (*A*)	*A* position			Distance (Å) *D*···*A*	Distance (Å) H···*A*	Angle (°) H···*A*···*D*
O(4)	O(2)	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$	2·549	1·70	4
O(2′)	O(3′)	$-x$	$-\frac{1}{2}+y$	$-\frac{1}{2}-z$	2·719	1·94	6
O(3′)	O(2′)	x	y	z	2·699	2·06	14
O(3′)	O(4)	x	y	$-1+z$	2·871	2·36	15
O(5′)	O(2′)	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$	2·858	1·99	7

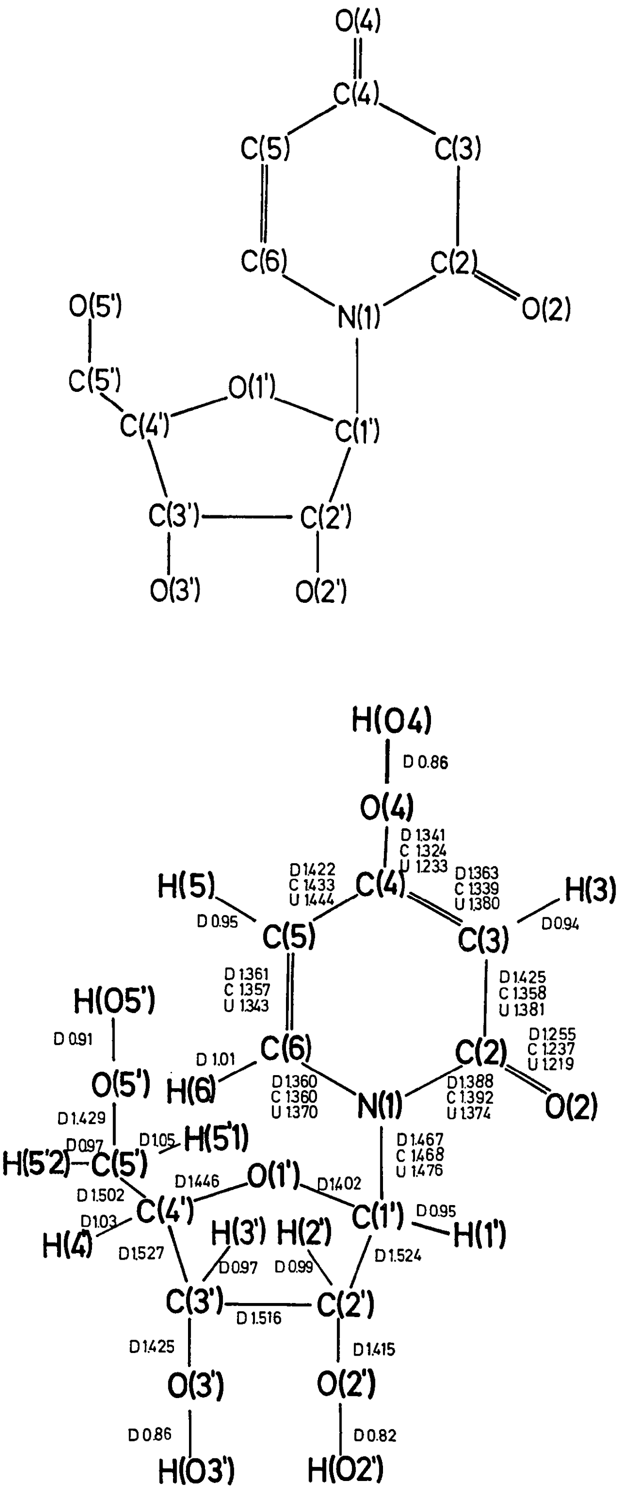


Fig. 1 Chemical structure, numbering convention, and bond distances in 3-deazauridine (D). Estimated standard deviations are 0·005–0·006 Å except when a hydrogen atom is involved, when it is 0·05–0·08 Å. Average distances in cytidine (C) and uridine (U) derivatives (Voet & Rich, 1970) are given for comparison; C(3) is replaced by nitrogen in both C and U, and O(4) is changed to nitrogen in C.

and adenosine (Boyd & Lipscomb, 1969, abbreviated BL). Two calculations were performed, one with the input parameters of JP and one with those of BL (Table 8; results labelled JP and BL respectively in Fig. 6). Atomic coordinates were taken from the crystal structure, overlap integrals S_{ij} for the Slater basis orbitals were calculated directly, diagonal Hamiltonian matrix elements H_{ii} were set equal to the negative of the corresponding valence state ionization potential (VSIP), and off-diagonal elements H_{ij} were approximated by the Wolfsberg & Helmholz (1952) equation $H_{ij}=0{\cdot}5\ K.S_{ij}.(H_{ii}+H_{jj})$ with $K=1{\cdot}75$ for JP and 2·00 for BL.

Table 8. *Input parameters for extended Hückel calculations on* 3-*deazauridine*

	Orbital exponent		VSIP (eV)			
	JP	BL	JP		BL	
	s,p	*s,p*	*s*	*p*	*s*	*p*
H	1·000	1·200	13·60		13·60	
C	1·625	1·625	21·40	11·40	21·40	11·40
N	1·950	1·950	26·00	13·40	26·00	13·40
O	2·275	2·275	35·30	17·76	37·59	14·62

The charge densities (Mulliken, 1955) calculated by these methods are presented in Fig. 6. Although the oxygen atoms attain a greater negative charge with JP parameters than with BL, there are no differences in the conclusions to be drawn. The base receives electron density from the ribose and carries a delocalized charge of −0·27 e for JP and −0·23 e for BL, virtually the same as the −0·27 e in C, −0·28 e in U, and −0·22 e in adenosine. Oxygen atom O(2) is definitely the most negative site in the molecule, followed by ribose

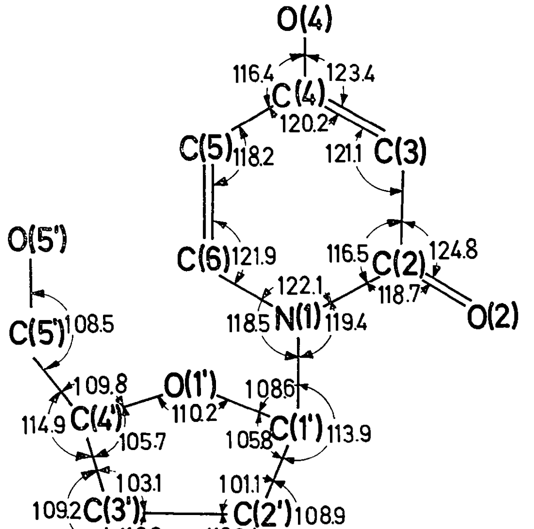


Fig. 2. Bond angles in 3-deazauridine (estimated standard deviations 0·3°).

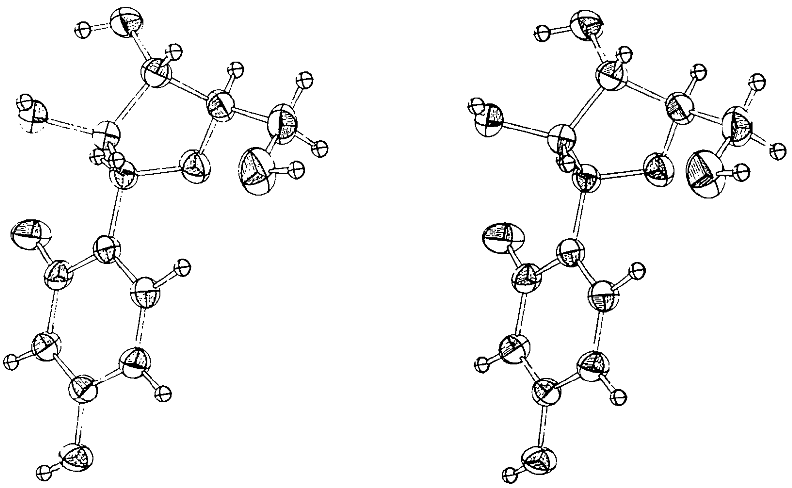


Fig. 3. Stereoview of 3-deazauridine drawn with the program *ORTEP* (Johnson, 1965). Thermal ellipsoids correspond to 50% probability.

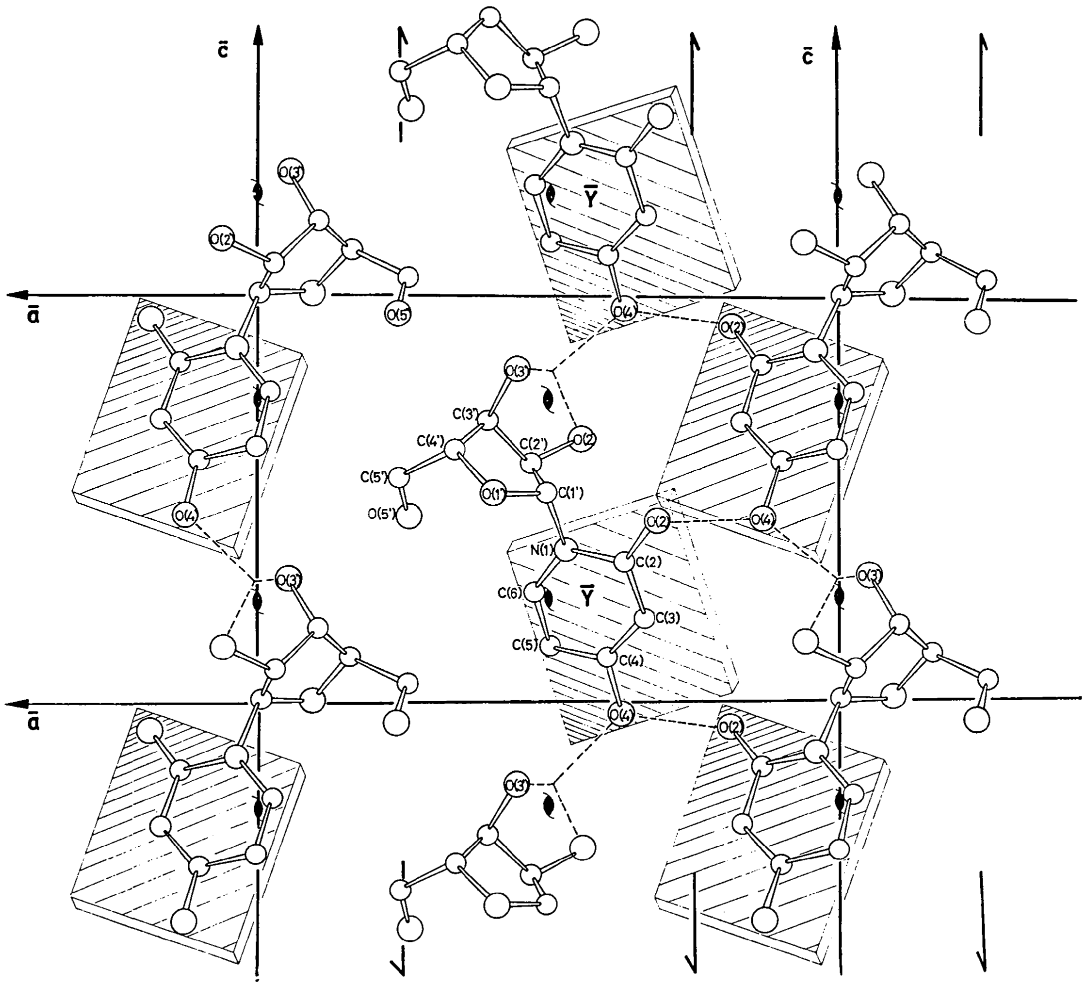


Fig. 4. Packing of molecules in the crystal as viewed along **b**. Molecules related by the screw axis with translation along **b** are not shown.

oxygens; O(4) is less negative. It is clear that O(2) can serve as an excellent hydrogen-bond acceptor for H(O4). The pattern of charges around the D heterocycle is not significantly different from C and U in the common C(5)–C(6)–N(1) portion. In D, carbon C(2) bears less of a positive charge than in C (+1·39 e) and U (+1·37 e). However, O(2) is similar in D, C (−1·42 e), and U (−1·42 e). At the 3-position of D the charge is similar to that on the imino nitrogen of U (−0·37 e) but not on the ring nitrogen of C (−1·02 e). On the other hand, conditions at the 4-position of D resemble those in C [+0·77 e on C(4), −0·67 e on N(4)] somewhat more than U [+1·18 e on C(4), −1·39 e on O(4)]. The H(O4) of D is more positive than either amino hydrogen of C (+0·36 e, +0·33 e).

Total overlap populations (Mulliken, 1955) show greater overlap to oxygen with BL than with JP parameters but excellent agreement otherwise (Fig. 6). The alternation in bond overlap population in the C–C bonds of the heterocycle follows that in bond distance; all these C–C bonds have greater overlap populations than the authentic C–C single bonds in the ribose. The overlap populations in the N(1)–C(2) and N(1)–C(6) bonds are almost equal despite the greater length of N(1)–C(2). The only unambigous changes in bond-overlap populations among D, C and U involve bonds where a substitution of atoms has taken place.

In summary, the polar groups of D resemble those of C but with enhanced polarity at site 4. The ring system has characteristics all its own. The possibilities

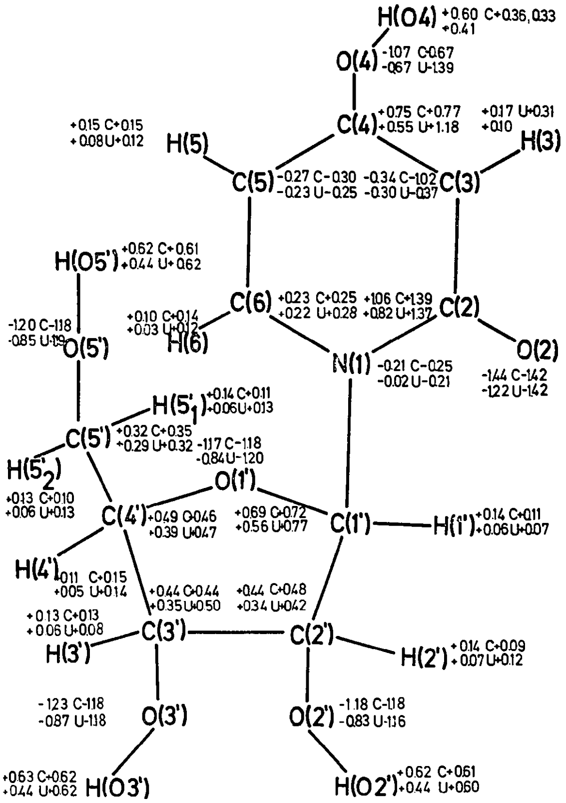


Fig. 6. Mulliken net charges for 3-deazauridine with JP (upper) and BL (lower) parameters, compared with those in C and U.

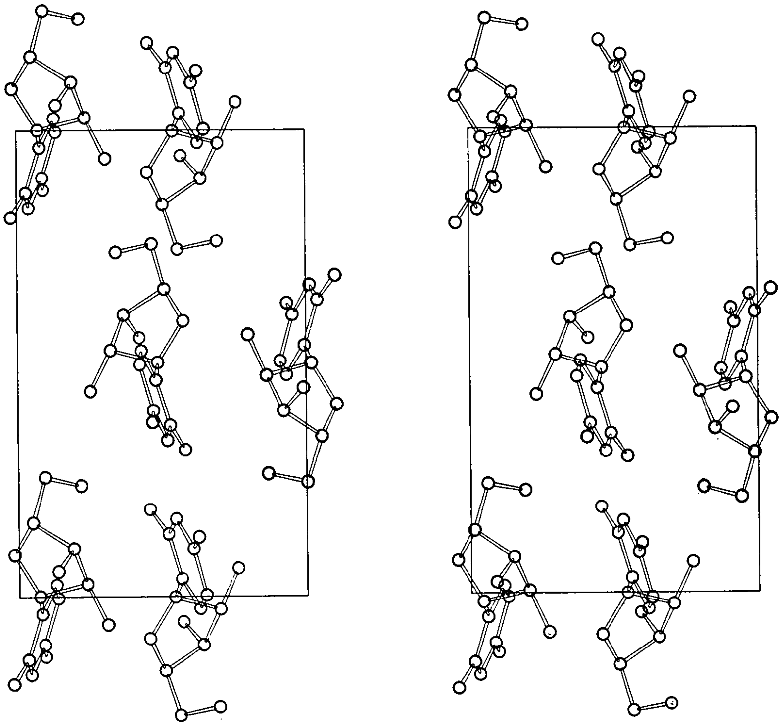


Fig. 5. *ORTEP* stereoview of the unit cell contents projected along **c**.

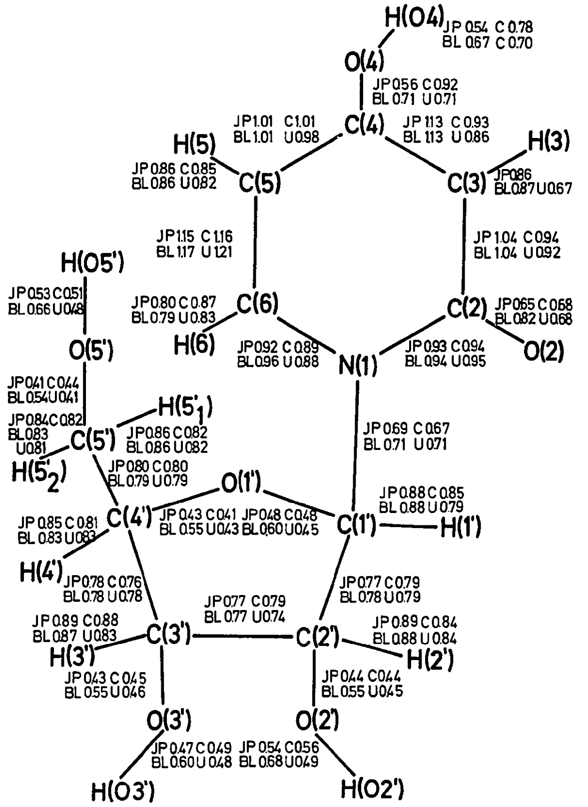


Fig. 7. Mulliken overlap populations in the bonds of 3-deaza-uridine with JP and BL parameters, compared with C and U.

for D to base pair with A, G and C have been discussed previously (Schwalbe, Gassen & Saenger, 1972).

We thank Professor Dr F. Cramer for his interest and support, Dr H. G. Gassen for generously providing the sample, Miss U. Wittenberg for valuable technical assistance, and Dr P. C. Manor for helpful discussions. Calculations were carried out on the UNIVAC 1108 computer at the Gesellschaft für wissenschaftliche Datenverarbeitung in Göttingen.

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