Packing

Fig. 6 shows the packing of beyerol monoethylidene iodoacetate viewed down the *a* axis. The molecules are stacked in pairs of parallel layers at 20° and 160° to the *c* axis. The end of the molecule containing the iodine atom is tightly packed, as are the three methyl groups. There are five intermolecular contacts less than 4·0 Å between the iodine and the other non-hydrogen atoms and six less than 3·70 Å between the carbon and oxygen atoms (Table 10). It is interesting to note that the closest nonbonded approach, O(2)···I (3·12 Å), is about 0·4 Å less than the sum of the van der Waals radii for iodine and oxygen. This is apparently due to the reduction of the iodine radius (Pauling, 1960) in the C(22)–I direction, the angle C(22)–I···O(2) being 175·5°.

The contact C(22)···O(3) may arise from an intermolecular C–H···O hydrogen bond (Sutor, 1960) although the evidence is inconclusive since the distance (3·44 Å) is rather long for a bond of this type. However, the hydrogen atom points towards O(3), being displaced from the C···O direction by only 19°, and C(22) is attached to the electronegative iodine atom which may enhance the possibility of hydrogen bond formation.

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The Crystal Structure of the Intermolecular Complex 9-Ethyladenine: 1-Methyl-5-bromouracil

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The crystal structure of a 1:1 complex of 9-ethyladenine with 1-methyl-5-bromouracil has been determined from three-dimensional X-ray diffraction data. The unit cell is triclinic and contains two base pairs. Two hydrogen bonds are found between the adenine and uracil derivatives involving uracil O(2) and N(3) and adenine N(6) and N(7). Pairs adjacent to each other are linked into infinite, flat, ribbon-like structures perpendicular to **a*** by another set of hydrogen bonds, between uracil O(4) and adenine N(6). There is an additional short nearest neighbor interaction between the bromine atom and the uracil O(2). The crystal is disordered and approximately 6% of the uracil residues have a different orientation with an alternative hydrogen bonding to adenine.

Introduction

The specificity of the hydrogen bonding between purine and pyrimidine bases in the nucleic acids is believed to underlie the stability of transmission and expression of genetic information. Deoxyribonucleic acid (DNA) is a double stranded polynucleotide structure in which the strands are believed to be held together through hydrogen bonds between the purines and pyrimidines (Watson & Crick, 1953). DNA replication, the manufacture of ribonucleic acid (RNA) and the synthesis of proteins are all believed to take place through the ordered and sequential interaction of purine and pyrim-

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idine bases. Although the general features of the structure of two-stranded polynucleotides have been established for DNA (Langridge, Marvin, Seeds, Wilson, Hooper, Wilkins & Hamilton, 1960), for RNA (Langridge & Gomatos, 1963; Tomita & Rich, 1964) and for synthetic polynucleotides (Rich, 1958; Davies, 1960; Rich, Davies, Crick & Watson, 1961; Langridge & Rich, 1963), the specific features of base pairing are difficult to obtain because of the cylindrical averaging which occurs in fiber X-ray diffraction patterns.

The mutagenic action of certain purine and pyrimidine derivatives has been interpreted on the basis of tautomeric shifts and 'rare' pairing configurations (Freese, 1963), the nature of which rests on a detailed understanding of the actual pairing configurations in DNA. One such derivative, 5-bromouracil, is an active mutagen when incorporated into DNA. The structural information we have relevant to these problems has come chiefly from single-crystal analyses of purines and pyrimidines, and recently, from crystals containing purine–pyrimidine complexes. The present work was undertaken to examine the effect of bromine on the hydrogen-bonding configuration of the pyrimidine ring. The results are compared with the related structures of the 9-methyladenine:1-methylthymine complex (Hoogsteen, 1959, 1963*a*), the 9-ethyladenine:1-methyluracil complex (Mathews & Rich, 1964) and the adenosine:5-bromouridine complex (Haschemeyer & Sobell, 1963). We find that the 9-ethyladenine:1-methyl-5-bromouracil crystalline complex has as its asymmetric unit a pair of bases held together by two hydrogen bonds, but with a configuration which differs from that seen in the complexes without the bromine atom. These results have been briefly reported (Katz, Tomita & Rich, 1965).

Experimental

Crystals containing a 1:1 complex of 9-ethyladenine and 1-methyl-5-bromouracil were prepared by dissolving equimolar amounts of the two bases in dimethyl sulfoxide with heating, and then allowing the solution to cool at room temperature. Crystals containing a 1:1 complex of 9-methyladenine and 1-methyl-5-bromouracil were prepared in a similar fashion. Small crystals were obtained and several with well-developed faces were selected for analysis. The mixed composition of the crystals was confirmed by dissolving them and measuring their ultraviolet spectrum and observing their behavior in paper chromatography (Table 1). This clearly showed a complex had formed. The unit cells of these crystals were determined from precession data with nickel-filtered Cu $K\alpha$ radiation (Table 2) and are distinct from those of the individual components. When the unit cells of the base pair crystals listed in Table 2 are transformed to correspond to the triclinic convention they are seen to be similar, and it will be demonstrated that these crystal structures are closely related. The densities of the ethyladenine:methylbromouracil and the methyladenine:methylbromouracil crystals were measured by flotation in a mixture of chloroform and bromoform and were 1·676 and 1·728 respectively. This corresponded very closely to the calculated densities for two base pairs per unit cell (1·698 and 1·769 respectively). The crystals of the methyladenine complex were of poor quality, and gave evidence for the presence of more than one lattice. They were not analyzed further. Weissenberg photographs of the ethyladenine complex were taken about the *c* axis and integrated Weissenberg photographs were taken about the *a* axis by the multiple-film technique. The reflections were indexed by using a computer program to calculate their positions on the Weissenberg films. Intensities were estimated visually; the data from a single film pack were put on a single scale and Lorentz–polarization corrections made with the use of the computer program XRDP-1 (Simpson, 1963). The data about the two axes were merged and put on a single arbitrary scale by a least-squares method (Rollett & Sparks, 1960). No absorption corrections were made since the crystals were less than 0·1 mm in size. A total of 3064 independent reflections were observed, representing 90% of the copper sphere. Of these, 511 were too weak to measure and were not included in the refinement or in the calculation of *R* values. One reflection was partially obscured by the beam stop, and 8 were judged to suffer from extinction. These 9 reflections were given zero weight in the refinement process. The reflections too weak to measure were assigned a value equal to one-half the minimum measurable intensity and corrected for Lorentz and polarization effects. The values obtained gave an estimate of the maximum magnitudes of the corresponding calculated structure factors. After completion of the refinement, the structure factors were computed for these reflections and compared with these estimates. No serious discrepancies ($F_{\text{cal}} > 2F_{\text{est}}$) were observed.

Solution and refinement

Solution of the structure was attempted by three-dimensional methods and was started from data obtained from the ($0kl$), ($hk0$), ($hk1$) and ($hk2$) zones. A three-dimensional Patterson synthesis was calculated

Table 1. *Chromatography of the intermolecular complexes 9-methyladenine:1-methyl-5-bromouracil and 9-ethyladenine:1-methyl-5-bromouracil*

Single crystals of each complex were isolated, then dissolved and analyzed.

Compound	R_f values Solvent 1	Solvent 2
9-Ethyladenine	0·64–0·66	0·88
9-Methyladenine	–	0·53
1-Methyl-5-bromouracil	0·47–0·48	0·29–0·33

Solvent 1: Isopropyl alcohol (85 ml), water (15 ml), concentrated ammonia solution (1·39 ml)

Solvent 2: 86% (v/v) aqueous n-butanol with 5% by volume concentrated ammonia solution (Wyatt, 1955).

using the Fourier summation program of Sly, Shoemaker & van den Hende (1962). It showed a large number of peaks in the $x=0$ and $x=\frac{1}{2}$ sections, indicating that the atoms were located in or near the planes $x=\frac{1}{4}$ and $x=\frac{3}{4}$. The bromine–bromine peak was located in the Patterson map near $x=\frac{1}{2}$, $y=0$, $z=0$, giving the trial bromine position. Assuming a center of symmetry, a three-dimensional Fourier synthesis was calculated using the phases based on the bromine atoms alone. The synthesis showed peaks for all the 21 non-hydrogen

Table 2. *Unit cell and space group data*

Crystal	Crystal system	Space group	*a*	*b*	*c*	*α*	*β*	*γ*	Number of molecules per unit cell
9-Ethyladenine + 1-methyl-5-bromouracil	Triclinic	$P\bar{1}$	7·908 ±0·025 Å	12·562 ±0·029 Å	8·680 ±0·014 Å	104·25° ±0·14	72·83° ±0·17	117·41° ±0·18	2 pairs
9-Methyladenine + 1-methyl-5-bromouracil	Triclinic	$P\bar{1}$	9·01	14·29	7·50	133·50	98·86	94·04	2 pairs
9-Ethyladenine + 1-methyluracil	Triclinic	$P\bar{1}$	7·74	8·39	12·33	107·84	63·65	105·25	2 pairs
9-Methyladenine + 1-methylthymine	Monoclinic	$P2_1/m$	8·30	6·55	12·84		106·83		2 pairs

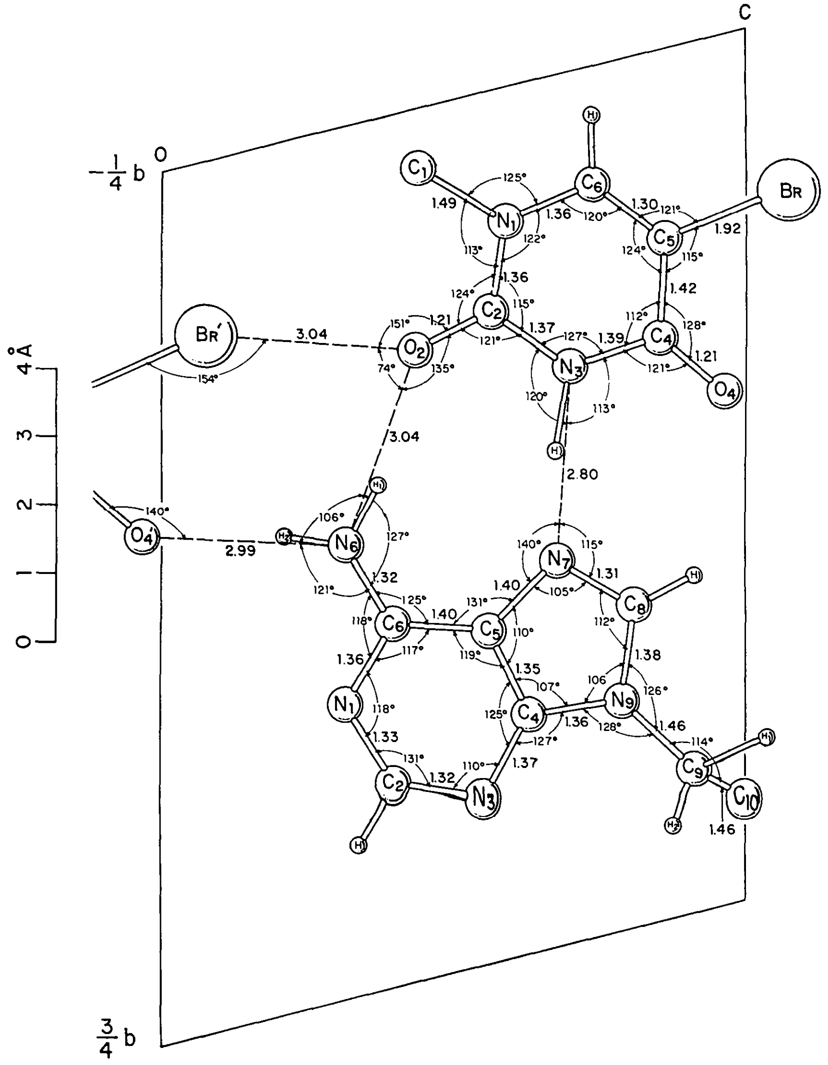
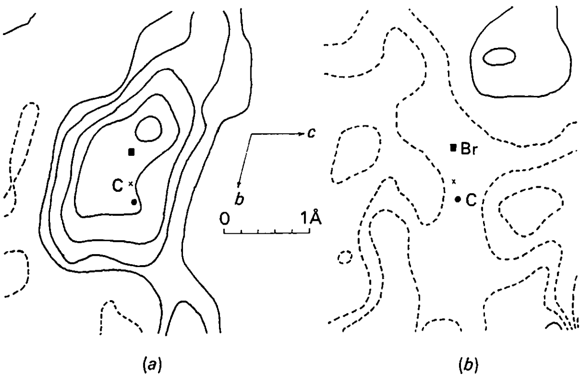


Fig. 1. Molecular arrangement of 9-ethyladenine: 1-methyl-5-bromouracil complex. One base pair is shown projected down the a^* axis. The estimated standard deviation in the bonds and angles shown is approximately 0·02 Å for covalent bonds, 0·025 Å for hydrogen bonds and 1° for all angles.

atoms in the asymmetric unit and revealed that the two molecules were forming a hydrogen-bonded pair (Fig. 1). A third Fourier synthesis, phased on atom positions determined from the second synthesis, was used to determine trial parameters for least-squares refinement.

The final merging of the intensities measured on 8 *a*-axis levels and 5 *c*-axis levels was used to determine a standard error, σ, associated with each reflection. The error, σ, was determined by a least-squares fit to the observed intensities (I) with an equation of the form $\sigma^2 = A + BI + CI^2$ (Hughes, 1941; Hoogsteen, 1963*a*). The values of $\sigma^2 = 4{\cdot}47 + 0{\cdot}144I - 4{\cdot}0 \times 10^{-7}I^2$ so obtained were used to calculate weighting factors $W = 1/\sigma^2$ in the last stages of refinement. Since the intensity scale used had been prepared with spots increasing in intensity by increments of 15%, the error corresponded to an error of estimation of ± 1 position on the intensity standard.

The least-squares refinement was based on minimizing a weighted residual formed from the observed and calculated F^2 values (Busing, Martin & Levy, 1963). The initial parameters obtained from the Fourier synthesis gave an R value based on F's which quickly refined to 22%. The atomic scattering factors for carbon, nitrogen, and oxygen were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and hydrogen from McWeeny (1951). The atomic scattering factor for bromine (Thomas & Umeda, 1957) was corrected for dispersion (*International Tables for X-ray Crystallography*, 1962) in later stages of refinement. Conversion to anisotropic temperature factors and further refinement yielded a stage where the parameter shifts were of the same order as the calculated uncertainties in the parameters. Calculation of interatomic distances and angles based on these parameters gave acceptable values, except for the methyl carbon to ring nitrogen [C(1)–N(1)] distance in the uracil molecule. This distance refined to 1·61 Å, compared with an expected value of 1·47 Å (Pauling, 1960). The discrepancy of nearly 0·14 Å was far outside the calculated probable error of 0·02 Å. A difference Fourier synthesis revealed a large volume of excess electron density in the neighborhood of but displaced from the expected position of the methyl group. It had a peak height corresponding to approximately 1·4 e.Å^{-3} [(Fig. 2(*a*)]. Since there should be three hydrogen atoms in this volume, it was initially thought that the omission of these atoms might account for the excess electron density and could cause the center of gravity of the carbon peak to shift outward from the uracil ring. Accordingly, trial positions for the hydrogen atoms were determined from small maxima in the difference map, but refinements showed that the omission of the hydrogen atoms was not responsible for the anomalously long bond.



(*a*) (*b*)

Fig. 2. (*a*) Section of the difference Fourier synthesis in the neighborhood of the uracil methyl carbon atom before considering disorder in the position of the uracil ring. (*b*) The same section after refinement with the inclusion of the uracil disorder. Contours are plotted at intervals of approximately 0·2 e.Å^{-2} with the contours at 0, ± 0·2 e.Å^{-2} omitted. Positive contours are solid; negative contours are dashed. The cross shows the position of the methyl carbon atom prior to the refinement for disorder. The black circle and square show the position of the methyl carbon and bromine atoms respectively after the refinement.

However, it was noted that a pseudo twofold axis of symmetry exists in the uracil derivative through the atoms N(3) and C(6) (Fig. 1). This arises, in part, because the van der Waals radius of the methyl group on N(1) is approximately the same as that for the bromide atom attached to C(5). A rotation of 180° about this axis also results in interchange of the two carbonyls O(2) and O(4); and of the ring atoms N(1) and C(5). If the uracil molecules in the crystal were randomly distributed in these two configurations, with most of them in the form revealed by the initial solution of the structure, then to a first approximation, the major effect observable in the Fourier synthesis would be a composite peak in the methyl region. For two forms present in the ratio 95% to 5%, the peak on the difference map would have a height near 1·4 e.Å^{-3}. The center of gravity of the peak would also be shifted away from the ring, as the bromine-ring carbon distance is near 1·9 Å. The effect on the bromine peak and of the C(5) and N(1) peaks on each other would be negligible at a 5% occupancy factor. This type of disorder has been seen previously in crystals of 2-amino-4-methyl-6-chloropyrimidine (Clews & Cochran, 1948), where a 50–50 mixture of two configurations (chlorine–methyl interchange) was found, with an average chlorine–methyl peak and an average bond distance. The possibility of these two alternative pyrimidine orientations was also considered by Hoogsteen (1963*a*, *b*), for 1-methylthymine and for the thymine–adenine complex, but it would not have been detectable in his analysis at the 5% level (K. Hoogsteen, personal communication), since this would have changed the ring carbon [C(5)] and nitrogen [N(1)] electron densities by only 0·05 e.Å^{-3}.

A refinement was then carried out by adding a second bromine atom with an isotropic temperature factor of 4·0 and a weight of 0·05, placed at the position of maximum excess electron density. The weight of the methyl carbon atom was correspondingly reduced to

Table 3. *Observed and calculated structure factors*

The columns contain, from left to right, *h*, *k*, $10F_{\text{obs}}$, $10F_{\text{cal}}$. The sign of F_{obs} has been set equal to the sign of F_{cal}. The reflections 400, 010, 020, $2\bar{2}0$, $\bar{2}11$, $2\bar{4}1$, $0\bar{4}1$ and 461 were judged to suffer from extinction. The 200 reflection was partially obscured by the beam stop and could not be estimated accurately. The above mentioned 9 reflections were given zero weight in the refinement process. At the end of the table are the unobserved reflections. This part of the table contains *h,k,l* (whenever necessary), $10F_{\text{min}}$ and $10F_{\text{cal}}$. F_{min} is the value of *F* calculated from one-half the minimum readable intensity, after correction for Lorentz and polarization effects. The sign of F_{cal} is affixed to F_{min}.

L = 0

1	0	-36	-35
2	0	-1066	-2237
3	0	63	63
4	0	761	797
5	0	-58	-54
6	0	-273	-248
7	0	31	28
8	0	67	71
0	1	144	354
1	-1	331	441
1	1	-224	-280
2	-1	-294	-274
2	1	-341	-433
3	-1	-343	-387
3	1	153	160
4	-1	212	221
4	1	267	289
5	-1	153	161
5	1	-62	-65
6	-1	-124	-118
6	1	-149	-127
7	-1	-52	-45
7	1	31	23
8	-1	50	48
8	1	36	43
0	2	613	937
1	-2	357	394
1	2	-399	-449
2	-2	-848	-1098
2	2	-418	-509
3	-2	-135	-53
3	2	200	208
4	-2	687	705
4	2	219	223
5	-2	-49	-33
5	2	-78	-75
6	-2	-319	-307
6	2	-81	-76
7	2	36	24
8	-2	85	103
0	3	432	534
1	-3	124	121
1	3	-117	-114
2	-3	-369	-378
2	3	-259	-318
3	-3	-123	-108
3	3	100	112
4	-3	131	142
4	3	144	144
5	-3	77	78
5	3	-69	-77
6	-3	-49	-69
6	3	-67	-64
7	-3	-36	-44
7	3	48	34
0	4	163	204
1	-4	57	42
1	4	-78	-81
2	-4	-200	-201
2	4	-140	-155
3	-4	-53	-78
3	4	79	89
4	-4	184	174
4	4	64	72
5	-4	22	21
5	4	-45	-40
6	-4	-108	-113
6	4	-20	-15
7	-4	22	24
0	5	271	332
1	-5	356	369
1	5	-322	-373
2	-5	-345	-354
2	5	-233	-274
3	-5	-92	-98
3	5	163	184
4	5	136	154
4	-5	355	310
5	-5	-36	-27
5	5	-63	-62
6	-5	-179	-167
6	5	-67	-62
7	-5	28	20
7	5	19	18
0	6	109	134
1	-6	176	195
1	6	-137	-153
2	-6	-174	-171
2	6	-34	-50
3	-6	-117	-133
3	6	87	93
4	-6	142	137
5	-6	59	68
5	6	-34	-41
6	-6	-90	-93
6	6	-17	-4
7	-6	-27	-25
0	7	215	253
1	-7	98	103
1	7	-82	-83
2	-7	-313	-318
2	7	-125	-131
3	-7	-144	-155
3	7	71	74
4	7	40	46
4	-7	263	237
5	-7	114	117
5	7	-40	-42
6	-7	-136	-123
6	7	-23	-6
7	-7	-38	-36
0	8	57	76
1	-8	158	152
1	8	-107	-103
2	-8	-126	-133
2	8	-39	-43
3	-8	-149	-135
3	8	65	39
4	-8	166	169
5	-8	97	93
5	8	-17	-11
6	-8	-121	-120
7	-8	-60	-51
0	9	53	57
1	-9	134	133
1	9	-137	-148
2	-9	-126	-121
2	9	27	14
3	-9	-42	-54
3	9	97	95
4	-9	139	123
4	9	-39	-31
6	-9	-89	-85
0	10	-49	-60
1	-10	-38	-29
1	10	51	54
2	10	54	50
3	-10	-43	-62
4	10	-26	-29
5	-10	106	109
6	-10	-48	-35
7	-10	-85	-75
1	-11	118	117
1	11	-81	-82
2	-11	-26	-30
3	-11	-79	-83
3	11	46	35
4	-11	53	47
6	-11	-26	-34
1	-12	20	7
1	12	-26	-4
2	-12	25	36
4	-12	-67	-45
5	-12	17	19
6	-12	29	21
7	-12	-17	-29
1	-13	97	91
1	13	-50	-59
2	-13	-23	-47
3	-13	-127	-116
4	-13	59	55
5	-13	97	97
6	-13	-27	-38
7	-13	-37	-44
1	-14	83	97
2	-14	19	13
3	-14	-116	-114
5	-14	99	95
6	-14	18	8
7	-14	-45	-58
2	-15	51	57
3	-15	-71	-80
4	-15	-67	-63
5	-15	58	73
6	-15	41	42

L = 1

0	0	-205	-197
-1	0	-794	-332
1	0	217	235
-2	0	417	440
2	0	-149	-160
-3	0	183	190
-4	0	-241	-231
4	0	173	174
-5	0	-95	-97
5	0	-19	-39
6	0	-101	-91
-6	0	87	74
-7	0	54	42
7	0	22	14
0	-1	473	582
0	1	479	556
-1	-1	-145	-129
-1	1	-124	-109
1	1	-121	-118
-2	-1	-346	-416
2	-1	-359	-382
-2	1	-738	-758
2	1	-270	-313
-3	-1	172	188
-3	1	171	148
3	-1	-80	-73
3	1	187	215
-4	-1	195	204
4	-1	167	161
-4	1	519	512
4	1	179	185
-5	-1	-92	-113
5	-1	22	32
-5	1	-112	-116
5	1	-103	-112
6	-1	-56	-57
-6	1	-244	-226
6	1	-84	-75
-6	-1	-77	-76
-7	-1	55	47
7	1	42	35
-7	1	70	71
-8	1	65	77
0	-2	-234	-271
0	2	251	255
-1	-2	-716	-723
1	-2	270	253
1	2	-205	-207
-1	2	166	162
2	-2	214	214
-2	2	-148	-151
2	2	-222	-251
-2	-2	-30	-45
3	-2	-48	-43
-3	-2	85	92
3	2	101	110
-4	-2	82	101
-4	2	47	53
4	2	147	155
4	-2	45	55
5	-2	-27	-35
-5	2	51	22
-5	-2	-37	-44
5	2	-62	-65
-6	-2	-52	-46
6	-2	-61	-72
6	2	-70	-65
-7	-2	32	24
7	-2	23	23
-7	2	-25	-19
7	2	41	37
0	-3	417	540
0	3	392	455
-1	-3	-51	-58
1	-3	65	36
1	-3	65	36
-1	3	174	199
1	3	-104	-170
-2	-3	-248	-296
2	-3	-443	-512
2	3	-160	-182
-2	3	-428	-398
-3	-3	38	49
-3	3	-167	-156
3	-3	77	65
3	3	64	69
-4	-3	117	117
-4	3	246	234
4	3	35	27
4	-3	209	268
-5	-3	-43	-32
-5	3	66	41
5	3	-39	-41
5	-3	-43	-51
-6	-3	-52	-39
-6	3	-153	-139
6	-3	-106	-116
6	3	33	7
-7	3	22	15
7	3	38	15
-8	3	51	66
0	-4	725	1002
0	4	333	385
-1	-4	-73	-71
1	-4	50	37
-1	4	26	46
1	4	-122	-130
-2	-4	-426	-522
2	-4	-809	-1059
-2	4	-461	-403
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3	-2	319	243
-3	2	-196	-194
3	2	258	207
-4	-2	39	39
4	-2	236	179
-4	2	35	47
4	2	49	39
-5	-2	33	38
5	-2	-181	-162
-5	2	75	84
5	2	-129	-106
6	-2	-113	-81
-6	2	-19	-31
7	-2	87	81
7	2	50	46
0	-3	220	233
0	3	118	119
-1	-3	50	44
1	-3	-105	-91
-1	3	272	213
1	3	-312	-299
-2	-3	-167	-145
2	-3	-301	-231
-2	3	-110	-123
2	3	-57	-48
3	-3	187	149
-3	3	-110	-112
3	3	303	275
-4	-3	51	54
4	-3	210	154
-4	3	57	63
-5	-3	15	10
5	-3	-154	-139
-5	3	40	45
5	3	-166	-164
6	-3	-98	-77
-6	3	-13	-19
7	-3	92	81
7	3	65	68
0	-4	94	97
0	4	-121	-128
-1	-4	138	136
1	-4	-214	-196
-1	4	74	75
1	4	-74	-71
-2	-4	-83	-76
2	-4	-112	-82
-2	4	71	66
2	4	144	123
-3	-4	-85	-59
3	-4	240	200
-3	4	-83	-84
3	4	54	66
-4	-4	39	41
4	-4	74	51
-4	4	-19	-5
4	4	-85	-81
-5	-4	12	17
5	-4	-183	-166
-5	4	59	67
5	4	-49	-42
6	-4	-39	-31
6	4	50	39
7	-4	136	110
0	-5	207	249
-1	-5	84	78
1	-5	-140	-130
-1	5	157	135
1	5	-112	-95
-2	-5	-130	-117
2	-5	-417	-374
-3	-5	-54	-34
3	-5	154	138
-3	5	-99	-97
3	5	38	42
-4	-5	39	45
4	-5	397	352
-4	5	20	28
5	-5	-114	-103
-5	5	33	42
6	-5	-237	-211
-6	5	-14	-16
7	-5	62	62
0	-6	205	219
-1	-6	-36	-41
1	6	-34	-27
-2	-6	-127	-115
2	-6	-252	-234
3	-6	59	51
-4	-6	26	37
4	-6	158	145
-4	6	-33	-1
5	-6	-79	-90
-5	6	-13	-14
6	-6	-44	-49
7	-6	66	76
0	-7	75	80
-1	7	94	87
1	7	-92	-92
-2	-7	-56	-43
2	-7	-154	-128
-3	7	-74	-79
3	7	74	66
4	-7	172	165
-4	7	49	51
4	7	-54	-4
5	-7	-37	-27
-5	7	53	61
6	-7	-155	-156
-6	7	-21	-34
7	-7	35	38
-1	-8	-107	-111
1	-8	136	127
-1	8	98	90
1	8	-72	-69
2	-8	-104	-101
-3	-8	54	67
3	-8	-77	-81
-3	8	-63	-64
3	8	47	39
4	-8	145	128
5	-8	18	14
6	-8	-79	-87
-1	-9	23	36
1	-9	-79	-72
-1	9	77	75
1	9	-39	-45
2	-9	45	56
2	9	43	24
3	-9	121	93
-3	9	-63	-76
4	-9	-73	-58
-4	9	-70	-17
[illegible]	-9	-74	-73
-5	9	31	49
6	-9	22	22
7	-9	34	41
0	-10	57	70
1	-10	40	37
-1	10	25	30
1	10	-33	-45
-2	-10	-44	-31
2	-10	-127	-107
4	-10	140	124
5	-10	-45	-34
6	-10	-110	-106
7	-10	58	55
-1	-11	-30	-17
2	-11	-56	-58
4	-11	94	81
5	-11	-47	-44
6	-11	-62	-70
7	-11	29	39
0	-12	75	76
1	-12	33	26
2	-12	-184	-139
3	-12	-48	-30
4	-12	237	177
5	-12	41	32
6	-12	-192	-159
1	-13	47	51
2	-13	-97	-78
3	-13	-86	-78
4	-13	116	99
5	-13	91	77
6	-13	-94	-95
7	-13	-36	-40
2	-14	-68	-74
3	-14	-79	-64
4	-14	115	104
5	-14	71	63
6	-14	-90	-101
7	-14	-34	-50
5	-15	27	30
6	-15	-58	-69
-2	11	27	19
4	-15	72	64
-4	10	-18	-4
L = 7			
-1	0	37	31
1	0	-70	-51
2	0	67	82
3	0	78	68
4	0	-117	-116
5	0	-57	-49
6	0	84	83
0	-1	67	70
-1	-1	80	79
1	-1	-121	-105
-1	1	-60	-55
1	1	58	68
-2	-1	-82	-62
2	-1	-52	-41
2	1	-92	-79
-3	-1	-56	-42
3	-1	139	108
-4	-1	26	35

Table 3 (*cont.*)

0·95. The final R value was the same as that obtained for the non-disordered form, but the carbon–nitrogen bond distance improved as well as did the difference map. On continued refinement, the carbon and bromine positions, their occupancies and temperature factors converged to the values shown in Table 4. The effect on the difference Fourier is shown in Fig. 2(*b*). In the refinement program, the sum of the bromine and C(1) occupancies was not constrained to total 1·0. However, the sum refined to a value close to 1·0, which reinforced our interpretation of the nature of the disorder. The final occupancy figure was near 94 % for the configuration seen in Fig. 1. Since the uracil ring is not exactly symmetrical about the N(3)–C(6) axis, further refinement would have to utilize two complete sets of uracil coordinates with fractional occupancies, and this was not attempted.

Trial positions for eight of the 14 hydrogen atoms in the asymmetric unit were then determined from a difference synthesis. Inclusion of these hydrogen atoms with isotropic temperature factors of 4·0 resulted in a decrease of the residual by 0·25%. Several cycles of refinement of the positions and anisotropic temperature factors of the hydrogen atoms and the associated heavy atoms were carried out. The final residual omitting the unobserved reflexions and those suffering from extinction was 12·7%. Several peaks were found near the methyl carbon atoms on uracil [C(1)] and adenine [C(10)] but they could not be unambiguously identified as hydrogen atoms. The observed and calculated structure factors from the last refinement cycle are presented in Table 3.

The final atomic coordinates determined by refinement of this disordered model are shown in Table 4. The calculated standard errors in atom positions and bond lengths and angles (Fig. 1 and Table 5) were based on the full variance–covariance matrix from the last cycle of the refinement (Busing, Martin & Levy, 1964). However, since the structure is disordered, these standard errors are probably too low, especially for the C(1)–N(1) bond in uracil.

Results

The crystalline complex formed by 9-ethyladenine and 1-methyl-5-bromouracil is nearly planar and is held together by two hydrogen bonds. The bond from the adenine amino group to the uracil O(2) has a length

Table 4. *Final atomic coordinates and anisotropic temperature coefficients**

	Atomic position			Anisotropic temperature factors × 10^4					
Atom†	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
*U*C(1)	0·2238 (19)	−0·1212 (16)	0·3990 (20)	390 (40)	22 (7)	273 (29)	78 (12)	−56 (27)	−6 (11)
[*U*Br]	0·2110 (34)	−0·1559 (27)	0·3794 (32)	465 (61)	48 (11)	373 (51)	118 (20)	−40 (45)	−13 (18)
*U*N(1)	0·2428 (12)	−0·0285 (6)	0·5456 (9)	284 (22)	62 (6)	124 (12)	71 (10)	−66 (13)	−5 (7)
*U*C(2)	0·2413 (15)	0·0738 (8)	0·5207 (11)	310 (28)	73 (8)	128 (15)	76 (12)	−59 (17)	1 (9)
*U*O(2)	0·2319 (13)	0·0896 (6)	0·3920 (9)	489 (28)	89 (7)	127 (11)	105 (11)	−91 (14)	17 (7)
*U*N(3)	0·2539 (13)	0·1605 (7)	0·6529 (9)	349 (25)	69 (7)	112 (11)	66 (11)	−81 (14)	8 (7)
*U*C(4)	0·2591 (15)	0·1525 (8)	0·8075 (11)	293 (26)	71 (8)	126 (14)	55 (12)	−67 (16)	11 (9)
*U*O(4)	0·2689 (13)	0·2359 (6)	0·9148 (9)	490 (27)	78 (6)	129 (11)	85 (11)	−111 (15)	−5 (7)
*U*C(5)	0·2544 (15)	0·0401 (9)	0·8168 (12)	272 (26)	95 (9)	147 (16)	63 (12)	−33 (17)	58 (10)
*U*Br(5)	0·2580 (2)	0·0198 (1)	1·0274 (1)	332 (3)	95 (1)	156 (2)	81 (1)	−82 (2)	36 (1)
*U*C(6)	0·2443 (14)	−0·0454 (8)	0·6943 (13)	232 (23)	76 (8)	182 (17)	63 (11)	−26 (16)	43 (10)
*A*N(1)	0·2291 (13)	0·4766 (7)	0·2704 (12)	332 (26)	72 (7)	196 (16)	70 (11)	−87 (17)	27 (9)
*A*C(2)	0·2541 (18)	0·5861 (9)	0·3489 (15)	412 (36)	66 (8)	211 (21)	81 (14)	−123 (22)	9 (11)
*A*N(3)	0·2807 (13)	0·6352 (6)	0·4978 (12)	310 (24)	52 (6)	223 (18)	63 (10)	−51 (17)	33 (9)
*A*C(4)	0·2752 (13)	0·5519 (8)	0·5774 (12)	214 (22)	65 (7)	173 (16)	54 (10)	−53 (16)	14 (9)
*A*C(5)	0·2473 (13)	0·4367 (7)	0·5136 (12)	218 (22)	59 (7)	123 (14)	52 (10)	−33 (14)	9 (8)
*A*C(6)	0·2222 (14)	0·3957 (8)	0·3532 (12)	240 (24)	63 (7)	149 (15)	49 (11)	−50 (16)	13 (9)
*A*N(6)	0·1919 (14)	0·2852 (7)	0·2780 (11)	324 (27)	72 (7)	144 (14)	71 (11)	−59 (17)	−5 (9)
*A*N(7)	0·2531 (12)	0·3784 (6)	0·6290 (10)	271 (22)	59 (7)	140 (12)	52 (9)	−39 (14)	21 (7)
*A*C(8)	0·2862 (16)	0·4609 (8)	0·7566 (12)	306 (28)	67 (8)	135 (15)	58 (12)	−37 (17)	9 (9)
*A*N(9)	0·3008 (12)	0·5689 (7)	0·7306 (10)	242 (21)	66 (7)	158 (14)	43 (9)	−36 (14)	6 (8)
*A*C(9)	0·3316 (19)	0·6773 (10)	0·8494 (16)	376 (37)	69 (9)	194 (22)	43 (15)	−38 (24)	−5 (12)
*A*C(10)	0·1544 (24)	0·6758 (13)	0·9656 (19)	489 (48)	132 (14)	240 (29)	120 (22)	−52 (32)	−44 (17)
				Equivalent isotropic temperature factor					
*U*N(3)H	0·2489 (251)	0·2462 (110)	0·6128 (186)	8·8					
*U*C(6)H	0·2248 (167)	−0·1308 (96)	0·6963 (126)	4·1					
*A*C(2)H	0·2645 (194)	0·6451 (87)	0·2874 (132)	4·1					
*A*N(6)H(1)	0·2061 (158)	0·2369 (112)	0·3458 (154)	3·7					
*A*N(6)H(2)	0·1800 (191)	0·2552 (95)	0·1768 (169)	4·0					
*A*C(8)H	0·2936 (163)	0·4457 (92)	0·8584 (126)	2·6					
*A*C(9)H(1)	0·3548 (190)	0·6680 (105)	0·9711 (144)	4·1					
*A*C(9)H(2)	0·3880 (185)	0·7448 (90)	0·8026 (154)	3·8					

* The numbers in parentheses represent the estimated standard deviations obtained from the least-squares refinement (× 10^4). The temperature parameters are the coefficients of the expression $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)$.

† *U* and *A* stand for the uracil and adenine derivative, respectively. The atom numbering system is shown in Fig. 1. H stands for hydrogen atoms. [*U*Br] represents the bromine atom in the less populated position in the disordered structure. Occupancy factors were determined from the least-squares refinement as :*U*C(1), 0·931 ± 0·058; [*U*Br], 0·080 ± 0·008; *U*Br(5), 0·949 ± 0·005.

3·04 Å, while a shorter bond of 2·80 Å goes from the uracil N(3) to the adenine imidazole nitrogen [N(7)]. Adjacent pairs are also bonded by a 2·99 Å link between the other proton on the amino group and the uracil O(4′) of another pair. The infrared spectra of the crystals (made by the potassium bromide disc method), reveal three peaks at 3180, 3285 and 3360 cm^{-1}, which correspond respectively to the N–H stretching frequency of a 2·7 Å N–H···N hydrogen bond and of 2·98 and 3·06 Å N–H···O hydrogen bonds (Nakamoto, Margoshes & Rundle, 1955). These are in quite good agreement with the X-ray data. In addition to the hydrogen bonding interactions, there is also a short contact of 3·04 Å between the bromine atom and O(2) of uracil.

Least-squares planes were calculated for the ring atoms of the adenine and of the uracil molecules. The r.m.s. deviation of the atoms from the plane of the rings is 0·017 Å for adenine and 0·012 Å for uracil (Table 6). These are within the errors in atomic positions; the only atom whose deviation from the molecular plane is significant is the uracil O(2). The uracil plane is tilted 2·9° from the *b–c* crystallographic plane, while the adenine plane is tilted 9·1°. The orientation of the rings to each other is that of a combined twist and tilt out of coplanarity, resulting in a dihedral angle of 6·3°. The atoms which take part in the hydrogen bonding show the largest deviations from their own molecular planes, but they do not lie in the plane of the complementary base. The van der Waals distances between the sheets of base pairs are all near 3·4 Å; the shortest contact is 3·29 Å between the bromouracil O(2) and the C(2) in the uracil ring stacked above it.

The amino group of adenine is participating in two N–H···O hydrogen bonds, and both of them are longer than normal. This lengthening probably reflects the participation of both hydrogen atoms in separate bonds with a consequent weakening of each. The covalent bond lengths are in agreement with earlier determinations of the purines and pyrimidines. The short carbonyl distance of 1·208 Å seen in the C(4)–O(4) bond is probably a result of the electronegativity of the adjacent bromine withdrawing electrons from the ring and strengthening the double bond character of this bond.

It is clear that the uracil in this crystal, as in all others studied, is in the diketo form; the bond lengths seen here are only slightly longer than the calculated value for a carbon–oxygen double bond (C=O) of 1·20 Å (Vaughan & Donohue, 1952; Penfold, 1953). The near equality of the four C–N bonds at a value intermediate between single and double in the uracil (Pauling, 1960) points to considerable resonance in these bonds. Similar bond hybridization can be seen in the adenine rings.

The base pairs in the crystal lattice form a long, ribbon-like network through the hydrogen bond between adenine N(6) and an adjacent uracil O(4). There is an additional interaction in this ribbon between adjacent uracil residues through the Br′–O(2) contact. The 3·04 Å separation is significantly shorter than the sum of the van der Waals radii, 3·45 Å (Pauling, 1960). This is the same type of short halogen–oxygen interaction reported by Camerman & Trotter (1964) for 5-iodo-2′-deoxyuridine. The amino nitrogen atom involved in the hydrogen bond N(6)–H···O(2) is 0·4 Å out of the plane of the uracil ring. This deviation may

Table 5. *Additional bond lengths and angles*

The calculated errors include the effects of errors in the measurement of the unit cell

Bond lengths

Atom 1	— Atom 2	Length	Atom 1	— Atom 2	Length
Hydrogen atoms $\sigma=0\cdot15$ Å					
*U*N(3)	*U*N(3)H	1·23 Å	*U*C(6)	*U*C(6)H	1·02Å
*A*C(2)	*A*C(2)H	0·98	*A*C(8)	*A*C(8)H	0·97
*A*N(6)	*A*N(6)H(1)	1·00	*A*N(6)	*A*N(6)H(2)	0·88
*A*C(9)	*A*C(9)H(1)	1·17	*A*C(9)	AC(9)H(2)	0.89
Separation of ‘glycosidic’ carbon atoms $\sigma=0\cdot082$ Å					
*U*C(1)	*A*C(9)	9·562			
Bond to bromine in less populated position $\sigma=0\cdot032$					
*U*N(1)	[*U*Br]	1·848			

Bond angles

Atom 1	Vertex Atom 2	Atom 3*A*	Angle	Atom 3*B*	Angle
Side group $\sigma=10$					
[*U*Br]	*U*N(1)	*U*C(2)	118·76°	*U*C(6)	118·72°
Hydrogen atoms $\sigma=70$					
*U*C(6)H	*U*C(6)	*U*N(1)	112·2	*U*C(5)	127·3
*U*N(3)H	*U*N(3)	*U*C(2)	107·5	*U*C(4)	125·3
*A*C(6)	*A*N(6)	*A*N(6)H(1)	111·1	*A*N(6)H2	129·2
*A*N(9)	*A*C(9)	*A*C(9)H(1)	113·6	*A*C(9)H2	112·4
*A*C(2)H	*A*C(2)	*A*N(1)	117·3	*A*N(3)	111·3
*A*C(8)H	*A*(C8)	*A*N(7)	123·5	*A*N(9)	124·5

be associated with the uracil O(2) which lies below the molecular plane. Steric interference from the neighboring bromine also contributes to this distortion.

Fig. 3 shows the vertical stacking in two related crystal structures 9-ethyladenine:1-methyl-5-bromouracil and 9-ethyladenine:1-methyluracil. The view is approximately perpendicular to the plane of the bases and three levels of sheets can be seen. The stacking of the adenine derivatives is nearly identical. The six-membered rings of the purine half-overlap in one pair of layers, and the six- and five-membered rings overlap each other in the next layer. In the crystal structure of 9-methyladenine:1-methylthymine (Hoogsteen, 1963*a*), there is a similar stacking of adenine derivatives with only the six-membered rings overlapping. The relative orientation of the pyrimidine rings is different in these three crystal structures. A schematic view down the *b* axis is represented in Fig. 4. The dotted line represents the vertical stacking of adenine residues with uracil projecting out on alternate sides. These piles then interlock with the uracil molecules from the adjacent stacks in the alternating slots. This produces a compact, space-filling structure. However, since the vertical

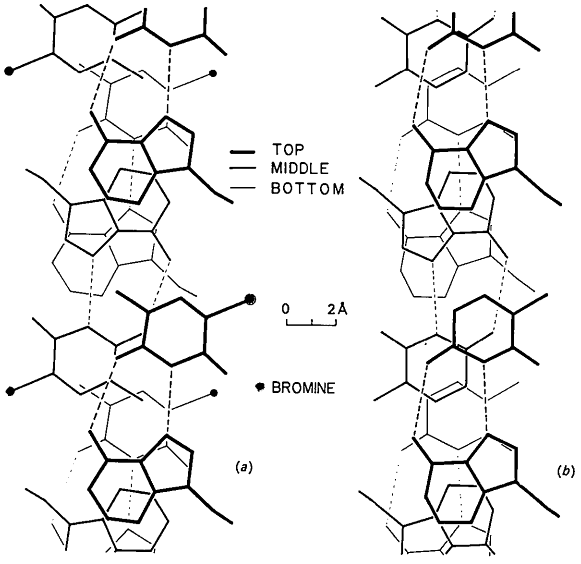

Fig. 3. The superposition of three layers in the crystal is shown to illustrate molecular stacking. The projection is viewed down the a^* axis. Intermolecular hydrogen bonds are shown as dashed lines. (*a*) Ethyladenine: bromomethyluracil. The bromine atoms are marked with dark circles. (*b*) The closely related structure ethyladenine: methyluracil (Mathews & Rich, 1964).

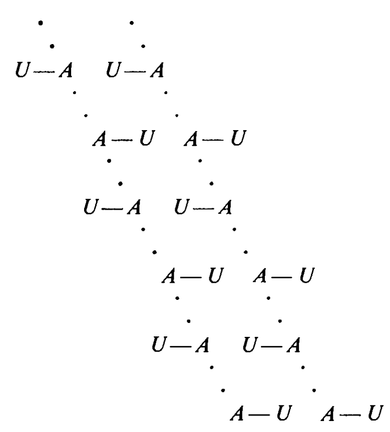

Fig. 4. Schematic view along the *b* axis showing the position of uracil residues relative to the overlapping adenines. Solid lines connect the hydrogen bonded pair. Dots represent the stacked adenines.

Table 6. *Least-squares planes*

The bromine atom of the uracil molecules in the minor-occupancy orientation is represented by [*U*Br]. The atoms in 9-ethyladenine are prefixed by *A*, in 1-methyl-5-bromouracil by *U*. Primed atoms are in neighboring base pairs. The number following the atom type represents the distance from the plane. These planes were calculated by the method of Blow (1960), and are given in terms of an orthogonal set of axes, where *Z* is parallel to *C*, and *y* lies in the *b–c* plane.

Uracil ring $0\cdot8759x+0\cdot4151y-0\cdot2460z=1\cdot5416$

N(1)	0·0294 Å	O(4)	0·0117 Å
C(2)	−0·0202	C(5)	0·0188
O(2)	−0·0628	Br(5)	0·0052
N(3)	−0·0001	C(6)	0·0140
C(4)	0·0042		

The r.m.s. deviation of the atoms in the plane is 0·0257 Å.

Distance of other atoms from this plane		Dihedral angle between this plane and	
*U*C(1)	−0·0288 Å	(100)	2·85°
[*U*Br]	−0·0975	(010)	67·69
*A*N(6)	−0·3995	(001)	75·76
*A*N(6′)	−0·6251		

Adenine ring $0\cdot8766x+0\cdot3472y-0\cdot3332z=0\cdot7590$

N(1)	0·0242 Å	N(6)	−0·0112 Å
C(2)	−0·0019	N(7)	−0·0027
N(3)	−0·0055	C(8)	0·0173
C(4)	−0·0125	N(9)	0·0113
C(5)	−0·0131	C(9)	−0·0075
C(6)	0·0015		

The r.m.s. deviation of the atoms in the plane is 0·0119 Å.

Distance of other atoms from this plane		Dihedral angle between this plane and	
*A*C(10)	−1·3351 Å	(100)	9·15°
*U*O(4′)	0·8966	(010)	72·48
		(001)	70·54

Dihedral angle between above two planes is 6·33°.
Least-squares plane fitted to an entire base-pair: $0\cdot8655x+0\cdot3968y-0\cdot3057z=1\cdot1359$.

*A*N(1)	−0·0399 Å	*A*C(9)	0·1267 Å
*A*C(2)	0·0107	*U*N(1)	0·1480
*A*N(3)	0·0566	*U*C(2)	0·0962
*A*C(4)	0·0100	*U*O(2)	0·1161
*A*C(5)	−0·0684	*U*N(3)	0·0370
*A*C(6)	−0·0999	*U*C(4)	−0·0348
*A*N(6)	−0·1889	*U*O(4)	−0·0934
*A*N(7)	−0·0777	*U*C(5)	−0·0083
*A*C(8)	0·0087	*U*C(6)	0·0611
*A*N(9)	0·0642	*U*Br(5)	−0·1239

The r.m.s. deviation of the atoms in this plane is 0·0885 Å.

Distances of other atoms from this plane		Dihedral angle between this plane and	
*U*C(1)	0·1776 Å	(100)	6·20°
[*U*Br]	0·1248	(010)	69·29
		(001)	72·20

packing of the uracil differs in the three structures described above, this may imply that a primary determinant in the structure in the unit cell is the adenine–adenine stacking interactions.

Discussion

This is the fourth report of an intermolecular complex of an adenine derivative crystallizing with a uracil (or thymine) derivative. In all of them, the pyrimidine N(3) is hydrogen-bonded to the adenine N(7), rather than to the adenine N(1) as suggested by Watson & Crick (1953) for DNA. It is quite likely that DNA uses the bonding to the adenine N(1) (Arnott, Wilkins, Hamilton & Langridge, 1965), probably because that is the only way a regular repeating structure can be assemled. Nonetheless, these alternative pairing arrangements may be found in other biologically important reactions, and are found in synthetic polynucleotide structures such as the three stranded helical form of polyadenylic acid + 2 polyuridylic acid (Felsenfeld, Davies & Rich, 1957). In the complexes of 9-methyladenine:1-methylthymine (Hoogsteen, 1959) and 9-ethyladenine:1-methyluracil (Mathews & Rich, 1964), the O(4) of uracil is bonded to the amino group of adenine, while in the adenosine:bromouridine complex (Haschemeyer & Sobell, 1963) the O(2) of uracil is used. In the present structure where steric considerations do not force the uracil ring into either configuration, 94% of the uracil derivatives are bonded to adenine through O(2) and only 6% through O(4). This suggests that the presence of the bromine atom may favor hydrogen bonding *via* O(2) perhaps by its inductive effect through the pyrimidine ring, which would tend to make O(2) more electronegative than O(4). It is difficult to assess the importance of this effect in view of the close bromine–oxygen contact described above, but if the effect is a significant one, it is possible that the alternative hydrogen bonding arrangement using uracil O(2) may be important in understanding the mutagenic role of bromouracil.

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