d'une part pour une liaison simple, d'autre part pour une liaison double assignant à l'atome d'hydrogène une position inverse de celle constatée pour l'acide N-α-naphtylchloro-4-phtalamique. L'acide N-α-naphtylchloro-4-phtalamique est actif en ce sens qu'il inverse le géotropisme naturel alors que l'acide N-α-naphtyltétrahydro-1,2,3,6-phtalamique ne l'est pas. Il convient d'attendre la résolution des structures cristallines d'autres acides arylphtalamiques pour envisager une relation structurale entre ces composés et l'hormone dont ils inhibent le transfert, à savoir l'acide β-indolylacétique dont la structure cristalline a été récemment publiée (Karle, Britts & Gum, 1964).

Les corrections préliminaires ont été effectuées sur machine CDC 3600, les autres calculs étant faits à la main et les séries de Fourier étudiées au photosommateur (von Eller, 1955, 1965.)

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The Crystal Structure of 5-Nitrouracil Monohydrate

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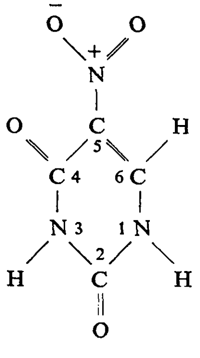
The crystal structure of 5-nitrouracil monohydrate is monoclinic with space group $P2_1/c$. The lattice translations are $a=5{\cdot}137$, $b=21{\cdot}956$, $c=9{\cdot}587$ Å, $\beta=143°30'$ with four formula units per cell. The structure has been determined from three-dimensional X-ray diffraction data measured in part from integrated Weissenberg photographs and, in part, using a diffractometer. The R value is 6% and the e.s.d.'s in positional parameters for the heavier atoms are about 0·0024 Å. Molecules of 5-nitrouracil are in the 2,4-dioxo tautomeric form. The dihedral angle between the plane of the pyrimidine ring and the nitro group is 4·7°. Both the water and the 5-nitrouracil molecules are linked by hydrogen bonds into sheets, these being separated by 3·05 Å. The water molecule is surrounded by five oxygen atoms and one imine group in an almost coplanar configuration. The water oxygen atom accepts a bent hydrogen bond from the imine group and the two water hydrogen atoms are involved in weak hydrogen bonds with four oxygen acceptor atoms. A hydrogen bond C(6)H(6)···O to a nitro oxygen atom (H···O, 2·30 Å) appears to be an important structure-determining factor.

Introduction

Interest in 5-nitrouracil (I)* has centered on its action as an analog for the naturally occuring pyrimidine bases uracil and thymine; *e.g.* Agren (1954) and Teramoto, Hashida & Mukai (1958) report it to be a bacterial growth inhibitor while Sormova, Melichar & Sorm (1960) report it to be a plant growth stimulant. Sebesta, Bauerova & Sormova (1961) give evidence that 5-nitrouracil is a competitive inhibitor in the enzymatic degradation of uracil by an extract of rat liver.

The crystal structure of 5-nitrouracil monohydrate has been undertaken in order to determine the tautomeric form of the molecule and the nature of the hydrogen bonding.



(I)

Experimental

The crystal data are given in Table 1. Colorless crystals of prismatic habit were readily grown by slow evaporation of the pale yellow aqueous solution. The crystals slowly effloresce at normal room temperature and

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* In this paper, atoms are numbered according to chemical convention, as in (I). Ring substituent atoms take the number of the corresponding ring atom, except for the nitro oxygen atoms, O(7) and O(8). The water molecule atoms are O(W), H(1, W), H(2, W).

humidity. Some care was needed in selecting and mounting crystals for data collection, since most crystals were found to be twinned or multiply twinned and very susceptible to slip parallel to the cleavage plane (100).

Table 1. *Crystal data for 5-nitrouracil monohydrate,* $C_4H_3O_4N_3.H_2O$

Monoclinic, M.W. 175·1
$a=$ 5·137 ± 0·005 Å $d_{100}=$ 3·049 ± 0·003 Å
$b=$ 21·956 ± 0·006 $\beta=$ 143° 30 ± 5′
$c=$ 9·587 ± 0·007 $U=$ 642 Å^3
$D_{\text{calc}}=$ 1·81 g.cm^{-3} $D_{\text{obs}}=$ 1·79 g.cm^{-3}
$Z=4$ formula units per cell. Space group $P2_1/c$.
Prominent crystal forms: {010}, {011}, {021}, {11$\bar{1}$}.
Cleavage plane: (100).

The diffracted intensity data for layers $h=0$ through 4 were recorded on integrated Weissenberg films with Cu $K\alpha$ radiation and estimated by means of a microdensitometer. The crystal used was elongated along **a**, with a cross section 0·21 × 0·26 mm. X-ray absorption factors were not applied since these were found to be essentially constant for a given value of h.

The data collection, including the measurement of the reported lattice parameters, was completed with a second crystal of dimensions 0·35 × 0·21 × 0·14 mm

Table 2. *Observed and calculated structure factors* (× 10) *for 5-nitrouracil monohydrate*

Asterisks mark unobservably weak reflections.

L= 0 H= 0		
2	40	36
4	253	266-
6	403	399-
8	273	283-
10	38	43
12	18	22-
14	83	87-
16	117	105
18	72	72-
20	66	60
22	243	243-
24	35	30
26	61	55-
28	83	81-
L= 1 H= 0		
1	210	221-
2	340	373
3	346	363
4	241	247
5	183	194-
6	94	93
7	478	508
8	535	579
9	366	367
10	84	80
11	247	255-
12	210	205-
13	129	123-
14	46	53
15	244	257-
16	98	104-
17	224	235
18	73	73
19	172	185-
20	91	90
21	18	19-
22	68	75-
23	80	82-
24	103	102
25	51	48-
26	44	44
27	17	16
L= 2 H= 0		
0	261	264
1	90	91
2	214	231-
3	107	109-
4	200	213
5	166	165
6	329	341-
7	202	207
8	162	161
9	88	90-
10	91	94
11	190	182
12	132	131
13	120	119-
14	19	1-
15	124	128
16	134	143-
17	356	382
18	157	156-
19	11	14
20	128	141
21	112	118-
22	52	56-
23	127	140-
24	40	37
25	58	66-
26	17	18
L= 3 H= 0		
1	198	206-
2	202	210-
3	41	44
4	3*	2
5	240	241
6	47	40-
7	69	71-
8	272	282
9	224	220-
10	160	158
11	33	33-
12	22	20
13	60	59
14	108	108
15	55	59-
16	11	7-
17	116	120
18	110	123-
19	13	14-
20	65	69-
21	133	141
22	44	47
23	24	22-
24	50	50
25	44	47
L= 4 H= 0		
0	109	113-
1	77	80-
2	230	240-
3	70	72-
4	99	104
5	119	119
6	46	45-
7	117	120
8	14	4
9	57	60-
10	22	21-
11	20	22-
12	118	121
13	24	20-
14	21	18
15	18	17
16	10	0
17	4*	6
18	4*	14-
19	20	16
20	10	11
21	28	29-
22	18	16
23	38	38-
L= 5 H= 0		
1	19	23
2	26	19
3	14	8
4	72	75-
5	54	54-
6	70	70-
7	24	24-
8	11	10-
9	82	87-
10	85	89-
11	76	80-
12	64	64
13	118	121
14	99	100
15	79	84
16	32	31-
17	47	56
18	47	52-
19	48	52-
20	7	7-
L= 6 H= 0		
0	12	8
1	12	9
2	27	27-
3	29	32
4	50	52
5	42	42
6	42	44-
7	4*	6-
8	37	38
9	12	11-
10	18	13
11	12	6
12	87	90-
13	103	110-
14	13	13-
15	36	40-
L= 7 H= 0		
1	3*	4
2	39	42
3	52	50-
4	71	72
5	8	3-
6	54	60-
7	50	54
L= -8 H= 1		
0	32	22-
1	46	41
2	31	13
3	77	74-
4	77	67-
5	152	140-
6	3*	4
7	32	34
8	8	3
9	26	23
10	23	19-
11	59	63
L= -7 H= 1		
1	4*	8-
2	94	86
3	67	53
4	139	122
5	19	18
6	142	130-
7	110	102-
8	104	94-
9	4*	0
10	13	7-
11	50	48-
12	32	28
13	90	90-
14	33	32-
15	112	112
L= -6 H= 1		
0	35	31-
1	19	19-
2	100	96
3	109	107
4	118	115-
5	39	28
6	44	39
7	49	41-
8	68	66-
9	43	36-
10	39	28-
11	4*	2
12	170	152
13	212	201-
14	46	38
15	69	70-
16	116	108-
17	12	15-
18	48	47
19	60	63
20	45	59-
21	80	75
L= -5 H= 1		
1	45	34-
2	54	45
3	4*	3-
4	212	187-
5	118	108
6	129	120-
7	58	63
8	65	59-
9	158	152
10	184	175-
11	134	128
12	123	115
13	216	204-
14	84	77
15	174	155-
16	19	20-
17	98	99-
18	94	92-
19	92	91
20	4*	0
21	4*	11-
22	34	32
23	40	47
L= -4 H= 1		
0	310	303
1	223	224-
2	439	455
3	49	49-
4	151	145-
5	164	147
6	126	116
7	250	223
8	56	55-
9	165	150-
10	71	71
11	67	63-
12	196	189-
13	67	58-
14	63	55-
15	62	60
16	25	12-
17	25	16-
18	5*	9-
19	51	46
20	27	17-
21	55	59-
22	30	33-
23	41	37-
24	115	109-
25	26	27
26	95	103
L= -3 H= 1		
1	318	355
2	381	403-
3	17	3-
4	3*	1
5	370	363-
6	60	61-
7	169	156
8	502	467
9	398	347
10	237	215
11	22	19
12	34	43
13	99	89-
14	160	140
15	39	37
16	4*	2
17	184	177-
18	202	194-
19	5*	8
20	61	60-
21	206	187-
22	36	35
23	36	28
24	97	89
25	71	67-
26	9	14
L= -2 H= 1		
0	271	258-
1	22	15-
2	322	341
3	55	61-
4	253	248-
5	144	138
6	435	416
7	358	342
8	160	149-
9	177	170-
10	140	142-
11	314	273
12	183	164-
13	160	149-
14	4*	3-
15	206	191
16	158	156
17	462	417
18	181	155
19	5*	16
20	183	179-
21	153	155-
22	51	48
23	142	133-
24	51	41-
25	95	96-
26	26	24-
27	21	16-
L= -1 H= 1		
1	299	311
2	359	391
3	345	352-
4	195	208
5	204	214
6	105	105
7	457	477-
8	551	576
9	358	353-
10	100	91
11	219	224
12	146	142-
13	106	103
14	11	8
15	245	245
16	64	62-
17	219	219-
18	57	47
19	158	160
20	111	109
21	5*	11
22	87	92-
23	72	70
24	105	104
25	53	48
26	34	29
27	31	29-
L= 0 H= 1		
1	53	48-
2	50	39-
3	168	181
4	199	209
5	35	37-
6	268	284
7	51	56
8	196	207
9	10	6
10	28	27-
11	32	32
12	17	7
13	20	22-
14	46	52
15	27	25
16	70	68-
17	20	14-
18	24	30
19	41	45
20	50	49-
21	20	25-
22	190	193
23	5*	3
24	32	31-
25	8	10-
26	51	51
L= 1 H= 1		
1	76	78
2	172	175-
3	155	160-
4	105	112-
5	75	83
6	46	47-
7	285	277-
8	302	301-
9	208	206-
10	9	7-
11	158	150
12	169	163
13	111	106
14	49	43-
15	126	132
16	100	101
17	178	173-
18	70	68-
19	135	140
20	53	49-
21	27	23
22	33	32
23	57	59
24	71	71-
25	40	36
26	44	52-
L= 2 H= 1		
0	134	131-
1	56	58-
2	71	81
3	79	77
4	77	82-
5	100	100-
6	154	156
7	38	43-
8	87	84-
9	27	22
10	71	69-
11	74	63-
12	58	54-
13	79	78
14	4*	10-
15	48	48-
16	105	102
17	239	239-
18	115	107
19	17	21-
20	79	86-
21	71	68
22	35	37
23	96	103
24	18	19-
L= 3 H= 1		
1	91	92
2	75	69
3	50	49-
4	5*	2-
5	118	110-
6	36	34
7	5*	5
8	108	108-
9	113	108
10	76	75-
11	32	27
12	4*	2
13	29	26-
14	60	61-
15	54	50
16	12	7
17	63	59-
18	63	63
19	3*	5
20	52	52
21	69	71-
L= 4 H= 1		
0	21	25
1	29	24
2	105	91
3	77	62
4	48	48-
5	67	62-
6	5*	4
7	57	55-
8	27	18
9	27	22
10	12	11-
11	4*	2-
12	63	59-
13	4*	8
14	8	1-
15	3*	7
16	3*	12
17	2*	11-
L= 5 H= 1		
1	11	16-
2	4*	11-
3	3*	6-
4	27	26
5	21	21
6	37	36
7	3*	4
8	3*	4-
9	42	44
10	42	44
11	39	40
12	27	30-
L= -9 H= 2		
1	57	56
2	4*	11
3	60	66
4	156	155-
5	45	47-
6	25	16-
7	50	50-
8	13	10
9	3*	5
10	35	42
11	9	1
12	19	24-
13	6	3-
L= -8 H= 2		
0	79	83
1	57	50-
2	4*	7-
3	119	114
4	133	126
5	242	241
6	11	4
7	77	75-
8	22	23-
9	13	16-
10	53	49
11	135	137-
12	47	48-
13	22	20-
14	82	82-
15	3*	4-
16	28	27-
17	56	55
L= -7 H= 2		
1	16	20
2	146	149-
3	4*	10-
4	175	174-
5	51	48-
6	214	216
7	173	172
8	154	155
9	4*	8-
10	35	32
11	62	66
12	60	53-
13	152	151
14	62	60
15	184	186-
16	4*	7
17	24	24-
18	18	14-
19	99	86-
20	3*	0
21	100	94-
L= -6 H= 2		
0	44	49
1	96	98
2	148	154-
3	213	218-
4	182	184
5	12	17
6	4*	9
7	91	92
8	74	75
9	53	60
10	60	63
11	4*	3
12	223	225-
13	290	291
14	68	60-
15	84	91
16	113	117
17	63	60
18	66	71-
19	109	109-
20	82	79
21	87	77-
22	76	62
23	31	33-
24	40	39
L= -5 H= 2		
1	73	62
2	87	84-
3	12	10
4	281	289
5	137	141-
6	162	160
7	71	78-
8	126	119
9	195	204-
10	244	255
11	141	148-
12	139	145-
13	224	234
14	25	22-
15	211	211
16	11	5-
17	105	112
18	119	120
19	120	117-
20	13	15-
21	4*	7
22	35	37-
23	55	47-
24	17	12-
25	99	91
L= -4 H= 2		
0	389	385-
1	314	316
2	452	466-
3	18	20
4	101	102
5	97	89-
6	115	112-
7	275	268-
8	59	58
9	239	229
10	57	56-
11	85	87
12	156	167
13	88	89
14	91	89
15	73	73-
16	4*	6
17	37	34
18	28	30
19	68	66-
20	12	5
21	77	76
22	45	41
23	27	19
24	120	115
25	27	22-
26	114	109-
L= -3 H= 2		
1	282	303-
2	377	389
3	8	1-
4	26	30
5	248	261
6	46	45
7	134	129-
8	385	393-
9	339	335-
10	151	149-
11	17	7-
12	26	33-
13	96	88
14	115	110-
15	24	14-
16	4*	14-
17	172	172
18	215	218
19	20	9
20	29	35
21	149	146
22	24	28-
23	12	12-
24	101	99-
25	55	51
26	17	14-
L= -2 H= 2		
0	104	111
1	116	119
2	204	215-
3	3*	4-
4	102	117
5	50	51-
6	213	238-
7	196	218-
8	47	44
9	130	137
10	141	152
11	185	185-
12	91	98
13	110	120
14	23	19
15	147	157-
16	130	139-
17	276	295-
18	103	105-
19	14	26-
20	152	162
21	140	144
22	22	19-
23	80	87
24	27	26
25	73	84
26	26	28
L= -1 H= 2		
1	201	206-
2	205	211-
3	156	159
4	53	57-
5	100	106-
6	62	64-
7	224	237
8	295	300-
9	186	192
10	29	31-
11	101	102-
12	65	64
13	72	74-
14	36	35
15	113	119-
16	23	24
17	125	137
18	27	20-
19	90	97-
20	91	90-
21	4*	2-
22	63	67
23	41	41-
24	71	72-
25	33	36-
L= 0 H= 2		
1	28	27
2	38	33
3	132	134-
4	145	141-
5	28	28
6	112	119-
7	37	38-
8	106	110-
9	4*	4-
10	4*	4
11	15	17-
12	12	13
13	22	18
14	10	7-
15	10	14-
16	16	14
17	4*	10
18	31	25
19	46	49-
20	30	30
21	26	27
22	93	104-
23	3*	4-
24	23	28
L= 1 H= 2		
1	34	35-
2	88	89
3	52	53
4	26	30
5	29	29-
6	22	20
7	104	105
8	115	121
9	77	78
10	35	31-
11	65	65-
12	85	88-
13	64	66-
14	26	22
15	34	28-
16	64	67-
17	102	103
18	39	42
19	71	78-
20	21	21
21	14	22-
22	11	7-
L= 2 H= 2		
0	45	44
1	22	18
2	22	21-
3	39	38-
4	22	15
5	40	43
6	54	59-
7	4*	5-
8	31	34
9	4*	6-
10	47	49
11	23	21
12	17	12
13	50	50-
14	22	15
15	8	8
16	58	60-
17	104	118
18	55	56-
L= 3 H= 2		
1	36	41-
2	4*	15-
3	34	29
4	10	8
5	45	46
6	31	28-
7	19	9
8	25	32
9	28	48-
10	44	28
11	24	14-
12	15	8-
13	11	7
L=-10 H= 3		
0	55	44-
1	46	49-
2	4*	6
3	65	71-
4	46	57
5	4*	4
6	28	21
7	118	134
8	31	30-
9	10	6
10	3*	3
11	42	48
12	20	24-
13	55	54-
L= -9 H= 3		
1	80	87-
2	15	14-
3	86	92-
4	244	261
5	74	76
6	38	31
7	45	51
8	4*	5
9	4*	6-
10	49	54-
11	4*	3-
12	31	26

Table 2 (*cont.*)

13	23	18
14	62	60
15	32	33
16	3*	6-
17	6	0
L= -8 H= 3		
0	137	146-
1	44	51
2	4*	13-
3	130	140-
4	167	165-
5	293	314-
6	35	28-
7	118	126
8	68	69
9	4*	13
10	90	93-
11	191	206
12	87	91
13	37	36
14	84	91
15	4*	10
16	40	44
17	71	76-
18	22	18
19	24	18
20	72	78-
21	31	34
L= -7 H= 3		
1	28	27-
2	191	192
3	50	44-
4	186	188
5	65	63
6	238	243-
7	219	220-
8	178	182-
9	38	30
10	46	44-
11	75	79-
12	93	85
13	175	176-
14	70	69-
15	211	224
16	4*	6
17	39	44
18	4*	6
19	89	95
20	4*	4
21	125	124
22	35	31-
L= -6 H= 3		
0	20	16-
1	130	133-
2	114	116
3	251	247
4	192	178-
5	33	39-
6	67	64-
7	101	103-
8	57	53-
9	44	42-
10	90	93-
11	4*	6
12	250	248
13	303	297-
14	59	53
15	87	91-
16	69	72-
17	74	70-
18	62	71
19	119	120
20	62	65-
21	68	66
22	72	65-
23	32	40
24	39	36-
L= -5 H= 3		
1	78	75-
2	87	84
3	32	36-
4	218	219-
5	110	112
6	141	140-
7	35	37
8	116	110-
9	184	182
10	219	216-
11	124	124
12	104	109
13	167	171-
14	12	8
15	196	192-
16	19	16
17	74	80-
18	98	102-
19	105	106
20	30	28
21	9	9
22	28	24
23	41	37
24	17	14
25	61	68-
L= -4 H= 3		
0	230	211
1	220	210-
2	247	243
3	27	21-
4	28	33-
5	38	33
6	34	29
7	207	188
8	4*	6-
9	194	181-
10	22	13-
11	76	72-
12	70	71-
13	65	64-
14	81	78-
15	39	39
16	23	6
17	27	24-
18	23	17-
19	56	58
20	25	13
21	58	63-
22	29	28-
23	17	4-
24	80	81-
L= -3 H= 3		
1	141	136
2	214	199-
3	30	24-
4	52	48-
5	114	103-
6	20	11-
7	44	36
8	197	182
9	229	209
10	60	55
11	10	9
12	26	13
13	60	56-
14	56	59
15	4*	13
16	27	16
17	122	117-
18	184	172-
19	13	14-
20	24	20-
21	64	62-
22	33	33
23	3*	3-
24	67	69
L= -2 H= 3		
0	21	23-
1	111	106-
2	79	76
3	4*	2
4	34	27-
5	28	20
6	87	85
7	59	55
8	4*	0
9	62	59-
10	109	109-
11	76	73
12	36	33-
13	63	65-
14	23	20-
15	81	78
16	111	105
17	163	154
18	56	56
19	23	21
20	112	110-
21	99	97-
22	3*	0
23	35	41-
L= -1 H= 3		
1	111	111
2	107	109
3	63	66-
4	4*	4-
5	38	32
6	30	29
7	84	88-
8	120	114
9	89	80-
10	11	6-
11	37	34
12	39	32-
13	47	48
14	37	34-
15	31	31
16	13	12-
17	64	65-
18	3*	7
19	53	50
20	56	56
L= 0 H= 3		
0	299	310-
1	15	3-
2	11	16-
3	65	65
4	91	85
5	13	12-
6	41	36
7	13	12
8	51	56
9	4*	3
10	4*	4
11	4*	2-
12	16	17-
13	4*	7-
14	4*	5-
15	4*	1-
16	10	9
17	8	2-
L= 1 H= 3		
1	15	19
2	42	49-
3	12	20-
4	4*	8-
5	10	11
6	40	6-
7	46	36-
8	27	50-
9	33	24-
10	28	29
11	40	27
12	43	38
L=-11 H= 4		
3	80	79-
4	58	56-
5	17	19-
6	23	24-
7	19	22
8	24	28-
9	26	31
10	59	63
L=-10 H= 4		
0	43	41
1	51	52
2	4*	1
3	99	85
4	105	103-
5	4*	4-
6	31	26-
7	172	172-
8	28	33
9	19	11-
10	23	8
11	63	71-
12	25	19
13	67	62
14	52	49
15	91	87-
L= -9 H= 4		
1	82	85
2	10	10
3	99	96
4	293	308-
5	112	104-
6	51	47-
7	37	37-
8	26	10-
9	21	5
10	52	53
11	21	4
12	31	23-
13	24	27-
14	82	75-
15	24	29-
16	8	0
17	3*	4
18	3*	0
19	24	27
L= -8 H= 4		
0	131	131
1	36	39-
2	26	32
3	133	133
4	151	138
5	285	282
6	40	35
7	134	132-
8	109	103-
9	29	34-
10	116	108
11	234	193-
12	105	105-
13	55	54-
14	59	64-
15	12	12-
16	49	44-
17	78	80
18	11	11-
19	19	17-
20	78	74
L= -7 H= 4		
1	11	14
2	165	164-
3	32	33
4	141	141-
5	33	34-
6	189	175
7	198	184
8	150	145
9	51	47-
10	32	23
11	88	81
12	105	93-
13	149	137
14	44	43
15	191	184-
16	12	12-
17	46	49-
18	4*	4-
19	74	69-
20	3*	4
21	110	107-
L= -6 H= 4		
0	28	25-
1	82	76
2	45	42-
3	144	155-
4	110	106
5	12	10
6	58	58
7	59	61
8	27	25
9	5*	0
10	91	84
11	20	22-
12	195	186-
13	235	209
14	26	28-
15	80	74
16	23	21
17	31	32
18	45	47-
19	83	84-
20	36	37
21	55	49-
22	58	57
L= -5 H= 4		
1	55	51
2	71	61-
3	45	42
4	91	87
5	73	66-
6	84	80
7	4*	5
8	59	56
9	113	111-
10	120	114
11	88	85-
12	54	52-
13	94	89
14	24	26-
15	128	121
16	4*	12-
17	40	41
18	59	58
19	72	68-
20	21	25-
21	15	18-
L= -4 H= 4		
0	47	48-
1	101	91
2	88	84-
3	36	30
4	4*	2
5	23	18-
6	4*	3
7	96	95-
8	20	19-
9	80	84
10	51	44
11	52	43
12	18	13
13	21	21
14	48	44
15	10	5-
16	9	8-
17	4*	7
18	3*	2-
19	41	38-
20	19	18-
21	39	38
L= -3 H= 4		
1	46	46-
2	69	71
3	35	23
4	43	34
5	43	39
6	4*	2-
7	4*	5
8	66	61-
9	118	108-
10	12	15-
11	4*	9-
12	8	3-
13	32	26
14	36	30-
15	10	12-
16	7	11-
17	74	66
18	108	103
L= -2 H= 4		
0	4*	2
1	68	63
2	13	21-
3	4*	8
4	10	4
5	14	13-
6	33	29-
7	4*	4
8	4*	2-
9	26	16
10	56	60
11	26	26-
12	17	9
13	23	26
14	15	11
15	25	27-
16	56	66-
L= -1 H= 4		
1	60	58-
2	58	56-
3	35	33
4	21	12
5	3*	5-
6	35	12-
7	44	31
L=-10 H= 5		
0	42	38-
1	40	37-
2	13	5
3	83	82-
4	116	114
5	4*	5
6	22	14
7	141	144
8	22	20-
9	17	16
10	22	23-
11	39	53
L= -9 H= 5		
1	57	53-
2	4*	2-
3	77	73-
4	250	241
5	111	104
6	54	53
7	23	20
8	14	9-
9	4*	5-
10	38	44-
11	4*	2-
12	17	17
13	15	19
14	44	54
L= -8 H= 5		
0	68	63-
1	27	23
2	37	29-
3	105	101-
4	86	78-
5	187	181-
6	10	11-
7	94	88
8	93	87
9	46	50
10	78	76-
11	110	110
12	73	76
13	52	54
L= -7 H= 5		
1	15	4
2	99	98
3	5*	5
4	83	78
5	4*	2
6	100	92-
7	117	110-
8	90	87-
9	47	45
10	11	0
11	65	65-
12	71	69
13	76	80-
14	12	11-
15	105	112
L= -6 H= 5		
0	29	28
1	31	27-
2	18	11
3	69	65
4	52	48-
5	17	13
6	23	22-
7	25	25-
8	11	10-
9	25	21
10	64	57-
11	27	22
12	105	102
13	116	115-
14	10	10
15	54	50-
L= -5 H= 5		
1	23	22-
2	47	47
3	32	28-
4	25	23-
5	39	35
6	36	34-
7	27	18-
8	23	23-
9	56	52
10	49	47-
11	55	53
12	17	20
13	41	38-
14	41	27
14	28	27
L= -4 H= 5		
0	4*	6-
1	30	35-
2	19	26
3	25	23-
4	4*	4
5	16	12
6	3*	0
7	44	42
8	14	15
9	25	28-
10	35	34-
L=-10 H= 6		
0	32	35
1	22	23
2	10	16-
3	50	61
4	72	81-
5	12	4-
6	4*	1
7	75	80-
8	11	7
9	16	18-
10	27	26
L= -9 H= 6		
1	23	24
2	4*	2-
3	31	44
4	122	137-
5	56	74-
6	34	42-
7	12	9-
8	23	28
9	9	6
10	34	32
L= -8 H= 6		
0	12	19
1	13	12-
2	15	17
3	53	64
4	32	38
5	80	95
6	4*	8-
7	44	46-
8	51	51-
9	34	40-
10	36	38
L= -7 H= 6		
1	4*	9-
2	29	46-
3	11	18-
4	24	34-
5	9	8
6	31	41
7	47	55

along **a**, **b**, **c**, mounted along **b**, using a manual diffractometer and Cu $K\alpha$ radiation. The intensity data obtained from this crystal were the layers $h=0$, 5 and 6, all reflections (162) found to be unobservably weak in the photographic data, and about 200 randomly selected reflections from layers $h=1$ through 4. The latter were used in scaling the photographic data. The intensity data from the second crystal were corrected for X-ray absorption. A total of 1330 non-symmetry-related reflections were measured, of which 120 were unobservably weak. The latter were estimated as half the minimum observable value.

The determination of the structure

From a consideration of the space group symmetry and the very strong diffracted intensities $h00$, all atoms in this crystal structure must lie close to the plane $x=\frac{1}{2}$ (or $x=0$, depending on an arbitrary choice of origin). The phase problem was solved from the three-dimensional sharpened Patterson section $u=0$, by a combination of direct inspection and multiple minimum function techniques.

Since the [a] projection of the structure shows complete atomic resolution, the y and z parameters were first refined by difference Fourier methods using only the $0kl$ data. The determination of the x parameters followed straightforwardly by three-dimensional Fourier methods. At this stage, hydrogen atom positions were found from a difference Fourier synthesis.

Atomic positional and anisotropic thermal parameters for the heavier atoms, together with positional parameters for the hydrogen atoms were refined by a full-matrix least-squares procedure. Standard deviations in the observed structure amplitudes were assumed to be given by

$$\sigma(F)=0{\cdot}5+0{\cdot}05|F|\,.$$

The thermal parameters for the hydrogen atoms were assumed to be the same as those of the heavier atoms to which they are covalently bound. The cleavage plane reflections 100 and 200 were omitted from the calculations since they appeared to be severely affected by extinction. After five cycles of least squares, all parameter changes were insignificant. The final R value was 0·067 for all reflections and 0·062 omitting unobservably weak reflections.

Observed and calculated structure factors are listed in Table 2. In Table 3 are listed the final values with e.s.d.'s for the parameters of the atoms in the assumed crystal chemical unit. A final difference Fourier syn-

Table 3. *Atomic parameters with e.s.d.'s for 5-nitrouracil monohydrate*

Positional parameters are expressed as fractions of the lattice translations.
Thermal parameters are given by the expression $\exp\,[-(\beta_{11}h\ +\beta_{22}k\ +\beta_{33}l\ +2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	x $\sigma(x)$	y $\sigma(y)$	z $\sigma(z)$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	0·5246	0·12603	0·8272	0·100	0·00087	0·0210	−0·0006	0·041	−0·0005
	0·0007	0·00010	0·0004	0·003	0·00004	0·0007	0·0002	0·001	0·0001
C(2)	0·5215	0·06473	0·7921	0·098	0·00084	0·0220	0·0002	0·011	0·0002
	0·0009	0·00011	0·0005	0·003	0·00005	0·0008	0·0003	0·001	0·0001
O(2)	0·5303	0·02555	0·8829	0·216	0·00092	0·0441	0·0005	0·092	0·0008
	0·0009	0·00009	0·0004	0·004	0·00004	0·0009	0·0003	0·002	0·0001
N(3)	0·5068	0·05250	0·6457	0·106	0·00055	0·0224	−0·0001	0·043	0·0000
	0·0007	0·00009	0·0004	0·003	0·00004	0·0007	0·0002	0·001	0·0001
C(4)	0·5055	0·09358	0·5366	0·076	0·00065	0·0191	−0·0003	0·033	0·0000
	0·0008	0·00009	0·0004	0·002	0·00004	0·0007	0·0002	0·001	0·0001
O(4)	0·5078	0·07489	0·4174	0·134	0·00076	0·0289	−0·0004	0·057	−0·0003
	0·0007	0·00008	0·0003	0·003	0·00003	0·0006	0·0002	0·001	0·0001
C(5)	0·4995	0·15642	0·5817	0·079	0·00063	0·0181	0·0000	0·032	0·0001
	0·0007	0·00010	0·0004	0·003	0·00004	0·0007	0·0002	0·001	0·0001
N(5)	0·4760	0·20586	0·4753	0·096	0·00067	0·0227	0·0005	0·039	0·0002
	0·0007	0·00009	0·0004	0·002	0·00003	0·0007	0·0002	0·001	0·0001
O(7)	0·4859	0·19544	0·3538	0·265	0·00097	0·0544	0·0012	0·114	0·0010
	0·0010	0·00010	0·0005	0·005	0·00004	0·0011	0·0003	0·002	0·0002
O(8)	0·4432	0·25814	0·5068	0·172	0·00058	0·0357	0·0016	0·069	0·0007
	0·0008	0·00008	0·0004	0·003	0·00003	0·0008	0·0003	0·001	0·0001
C(6)	0·5126	0·16978	0·7256	0·078	0·00074	0·0201	−0·0003	0·033	−0·0002
	0·0008	0·00011	0·0004	0·003	0·00004	0·0007	0·0002	0·001	0·0001
O(*W*)	0·5045	0·10768	0·1118	0·126	0·00109	0·0284	0·0004	0·053	0·0000
	0·0007	0·00009	0·0004	0·003	0·00004	0·0007	0·0002	0·001	0·0001
H(1)	0·542	0·135	0·918						
	0·013	0·002	0·007						
H(3)	0·529	0·015	0·631						
	0·014	0·002	0·007						
H(6)	0·514	0·211	0·758						
	0·013	0·002	0·007						
H(1, *W*)	0·511	0·121	0·198						
	0·015	0·002	0·008						
H(2, *W*)	0·516	0·068	0·115						
	0·015	0·002	0·008						

thesis (Fig. 1) shows all the hydrogen atoms but no other significant residual electron density.

Discussion of the structure

(i) *The 5-nitrouracil molecule*

The nature of the tautomeric form of 5-nitrouracil in solution has been investigated by means of nuclear magnetic resonance (n.m.r.) and ultraviolet spectra. Kokko, Mandell & Goldstein (1962) found no signals in the n.m.r. spectrum of 5-nitrouracil in dimethyl sulfoxide solution which could be attributed to the interaction of the imine hydrogen atoms with H(6), from which it was concluded that these imine hydrogen atoms were significantly more labile than is the case for 5-bromouracil or thymine. From the ultraviolet spectrum of 5-nitrouracil in aqueous solution, Brown (1959) deduced that the molecule is predominantly in the 2,4-dioxo form (I). This is the form presently reported as existing in the crystalline monohydrate.

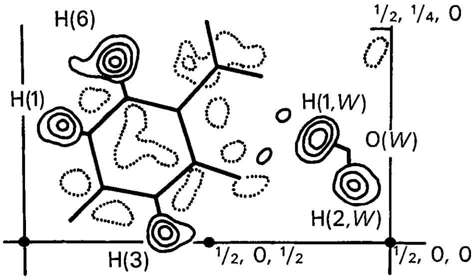


Fig. 1. Final difference Fourier synthesis in the section $x=\frac{1}{2}$, showing the hydrogen atoms. Contours are at intervals of 0·2 e.Å^{-3}. The zero contour is omitted and contours of negative electron density are shown dotted.

The pyrimidine ring is almost planar with a slight degree of boat configuration (Fig. 2 and Table 4). The atoms of the nitro group and C(5) are coplanar with a dihedral angle of 4·7° between this plane and the best plane through the six ring atoms. It can be seen from Fig. 3 that the thermal molecular motion is predominantly a translational vibration parallel to **a***, the ring normal. The only readily discernible intramolecular feature in thermal behavior is an oscillation of the nitro group about the axis C(5)–N(5). Since a proper estimate of the corrections to interatomic distances arising from anisotropic thermal motion cannot be made, the bond lengths and angles shown in Fig. 4(*a*) are those calculated directly from the reported positions of the thermal centroids (Table 3). However, Table 5 lists corrected bond lengths for 5-nitrouracil, giving both the minimum possible bond lengths and the bond lengths assuming the 'riding' mode of thermal motion (Busing & Levy, 1964). These corrections have little if any effect on the ring bonds, but suggest that the carbonyl and nitro N–O lengths in Fig. 4(*a*) may be underestimated by as much as 0·02 or 0·03 Å. The standard deviation in the ring bond lengths is estimated to be 0·006 Å and in a bond angle to be 0·4°. The e.s.d. in bond lengths involving hydrogen atoms is 0·06 Å.

Table 4. *Least-squares planes through atomic centers*

The planes $Ax+By+Cz=D$ are referred to the crystallographic axes.

Plane	*A*	*B*	*C*	*D*
1	0·61491	0·00392	−0·02560	1·45521
2	0·58333	0·07788	0·01161	1·82566

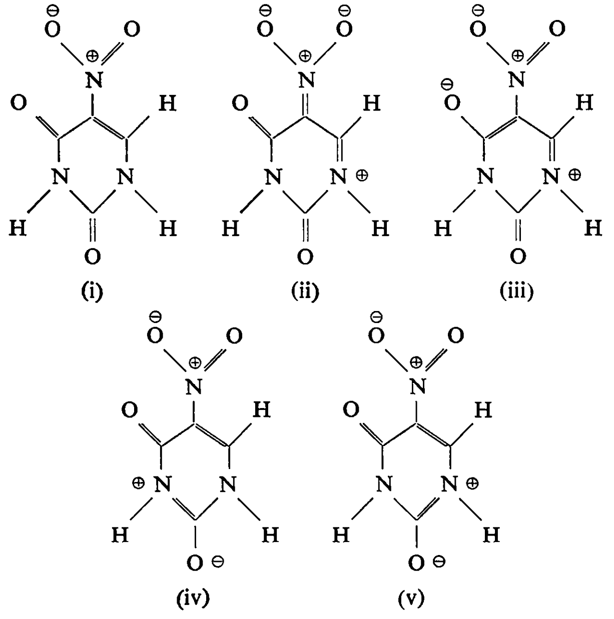
Dihedral angle $(1 \wedge 2) = 4{\cdot}7°$.

Distances of atoms from the planes*

Atoms forming the plane	Plane 1	Plane 2	Atoms not forming plane	Plane 1
N(1)	0·008 Å		H(1)	0·029 Å
C(2)	−0·001		O(2)	0·000
N(3)	−0·012		H(3)	0·027
C(4)	0·017		O(4)	0·049
C(5)	−0·011	−0·001 Å	N(5)	−0·054
C(6)	−0·001		O(7)	0·005
N(5)		0·003	O(8)	−0·159
O(7)		−0·001	H(6)	0·049
O(8)		−0·001		

* See also Fig. 2.

The observed bond lengths in 5-nitrouracil are compatible with a valence bond description of the molecule in which contributors (i) and (ii) predominate, with (iii), (iv) and (v) in a minor role.



(i) (ii) (iii)

(iv) (v)

It may be argued that (i) is favored over all other contributors in having only one formal charge separation, whereas (ii) is favored in view of the established electron attracting character of the nitro group.

Table 5. *Thermal corrections to the bond lengths in 5-nitrouracil*

Column (1) Distance between thermal centroids.
(2) Minimum possible bond lengths for the reported anisotropic thermal parameters.
(3) Bond lengths assuming the 'riding' mode of thermal motion.

	(1)	(2)	(3)
N(1)–C(2)	1·384 Å	1·384 Å	1·384 Å
C(2)–O(2)	1·199	1·202	1·222
C(2)–N(3)	1·370	1·370	1·370
N(3)–C(4)	1·377	1·377	1·382
C(4)–O(4)	1·224	1·225	1·236
C(4)–C(5)	1·453	1·453	1·453
C(5)–N(5)	1·427	1·427	1·431
N(5)–O(7)	1·228	1·235	1·263
N(5)–O(8)	1·232	1·234	1·251
C(5)–C(6)	1·358	1·358	1·358
C(6)–N(1)	1·334	1·334	1·335

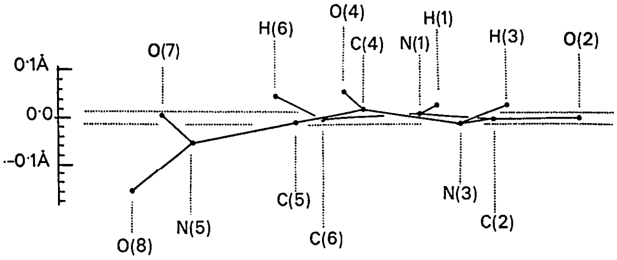


Fig. 2. The conformation of 5-nitrouracil in the monohydrate. Atomic displacements from plane (1) of Table 4 are shown with distance on the vertical scale 15 times that on the horizontal scale. The parallel dotted lines are at distances from plane (1) of three times the e.s.d. in the atomic positional parameters for the heavier atoms.

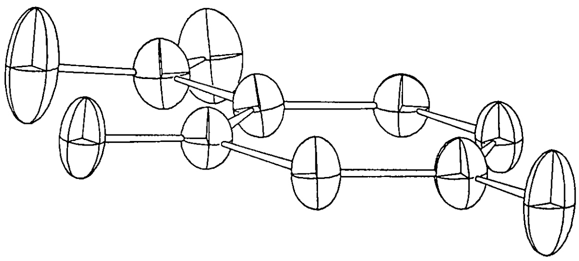


Fig. 3. The ellipsoid representation of atomic thermal parameters for the heavier atoms of the 5-nitrouracil molecule.

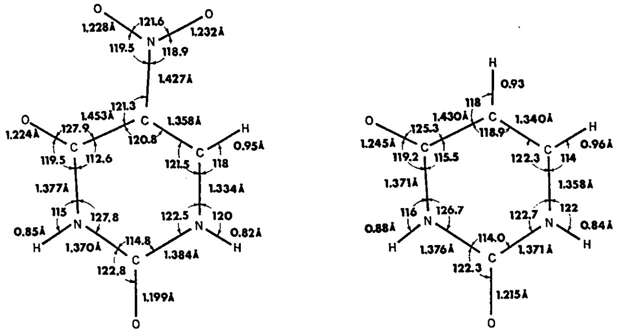


Fig. 4. Bond lengths and angles (uncorrected for thermal motion) in (left) 5-nitrouracil (present work) and (right) uracil (Stewart & Jensen, 1966).

It is of interest to examine the effect which nitro-substitution produces in the pyrimidine ring by comparing the bond lengths and angles for 5-nitrouracil [Fig. 4(*a*)], with those obtained for uracil [Fig. 4(*b*)] in a recent accurate X-ray redetermination (Stewart & Jensen, 1966). The e.s.d.'s in bond lengths and angles in the uracil ring are reported to vary between 0·0019 and 0·0026 Å and 0·1 and 0·2° respectively. These data are also uncorrected for the effects of thermal motion. The bond lengths C(4)–C(5), C(5)–C(6), C(6)–N(1), N(1)–C(2) are respectively longer (0·023 Å), longer (0·018 Å), shorter (0·024 Å), longer (0·013 Å) in 5-nitrouracil than in uracil itself, all differences being significant except possibly the last. Bond lengths C(2)–N(3) and N(3)–C(4) are essentially the same in both rings. These differences, except in the bond N(1)–C(2), can be qualitatively explained in terms of the importance of contributor (ii) to the valence structure of 5-nitrouracil and the absence of a corresponding contributor for uracil itself.

The differences in the ring bond angles in the two molecules are small, except for the closing of the angle at C(4) in 5-nitrouracil by 2·9°. This (together with the large angle C(5)–C(4)–O(4) of 127·9°) is probably the result of the intramolecular non-bonded repulsion O(4)···O(7), which has no counterpart in uracil.

Accurate crystal structure analyses have been carried out for the related molecules *N*-methylthymine (Hoogsteen, 1963) and thymine hydrate (Gerdil, 1961). As might be expected, bond lengths in *N*-methylthymine are very similar to those in uracil, but the bond lengths N(1)–C(2), N(3)–C(2) in thymine are shorter (1·355, 1·361 Å) and C(2)–O(2) probably longer (1·234 Å) than in either of the other structures, or in 5-nitrouracil. Hoogsteen (1963) suggests that these bond length differences are correlated with the strong N(1)···O(2) and N(3)···O(2) intermolecular hydrogen bonds in thymine hydrate. This feature is absent in the other three crystal structures.

The C(5)–N(5) bond length (1·427 Å) is longer than that in anhydrous 5-nitrobarbituric acid (1·407 Å; Bolton, 1963), being in the range of values reported for aromatic nitro compounds in which the nitro group is approximately coplanar with the ring atoms and for which contributors with C$=$N$^+$ such as (ii) can be written. These structures have been tabulated and discussed by Trotter & Mak (1965) and Coppens & Schmidt (1965).

(ii) *The water molecule*

The water molecule has O–H bond lengths of 0·84 and 0·88 Å and an angle H–O–H of 111°. These are typical values for an X-ray structure analysis.

(iii) *The molecular packing and hydrogen bonding*

Fig. 5 shows the structure of one hydrogen bonded sheet of 5-nitrouracil and water molecules. Intermolecular distances within a sheet which involve hydrogen atoms are given in Fig. 5. Other important distances and angles are listed in Table 6. Adjacent sheets are separated by a d_{100} spacing of 3·049 Å and are related by the lattice translation **a**. The strongest interactions between adjacent sheets are van der Waals, this being compatible with the observed perfect (100) crystal cleavage. The comparative looseness of the intersheet

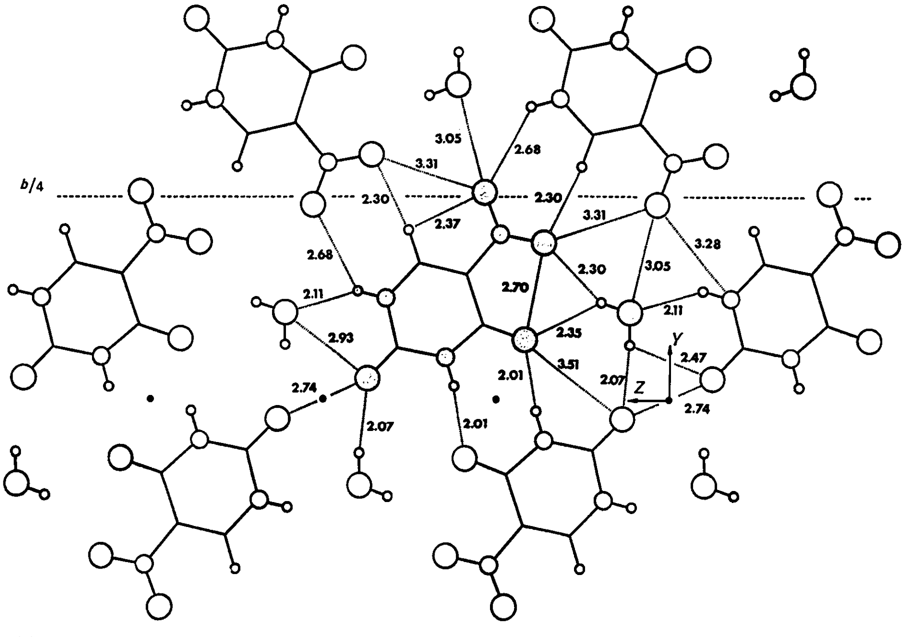


Fig. 5. Molecular packing and hydrogen bonding in 5-nitrouracil monohydrate. The sheet at $x=\frac{1}{2}$ is shown, viewed down **a***. Circles of decreasing radii represent oxygen, nitrogen and hydrogen atoms respectively. The shaded atoms belong to the assumed crystal chemical unit. The distances which are shown involving hydrogen atoms have an e.s.d. of about 0·06 Å. Other distances have e.s.d 's of about 0·006 Å.

packing near the nitro group oxygen atoms O(7), O(8) [Table 6, (iii)] undoubtedly facilitates the observed intramolecular thermal vibration of these atoms about the C(5)–N(5) axis.

Molecules of 5-nitrouracil are hydrogen bonded N(3)H(3)···O(4)′ in pairs across crystallographic centers of symmetry. The resulting dimers are further hydrogen bonded through water molecules to form almost coplanar ribbons parallel to **c**. The hydrogen bonding interactions C(6)H(6)···O(7)′ with distances C(6)···O(7)′ and H(6)···O(7)′ of 3·25 and 2·30 Å must be the principal attractive forces responsible for binding these ribbons to form almost coplanar sheets, since the inter-ribbon interactions N(1)H(1)···O(8)′ must be very weak with a distance N···O of 3·28 Å and a distance H···O (2·68 Å) comparable to the sum of the van der Waals radii for hydrogen and oxygen (2·6 Å) and with an unfavorable angle N(1)H(1)O(8)′ (131°) for hydrogen bonding.

In Fig. 5 it can be seen that the water oxygen atom has five oxygen and one imine nitrogen atom as near neighbours, all these atoms being almost coplanar and with oxygen atoms at distances from the central atom ranging between 2·92 and 3·03 Å. There are van der Waals contacts between the water oxygen atom and atom C(2) at 3·30 Å on one side of this plane and atoms C(4), C(5) at 3·07, 3·25 Å on the other side [Table 6(iii)]. There is also a short van der Waals distance O(2)···O(2)′ of 2·74 Å in the environment of the water molecule, a distance almost the same as that of the intramolecular non-bonded interaction O(4)···O(7), 2·70 Å. The water molecule accepts a bent hydrogen bond N(1)H(1)···O(*W*) with an angle 153° at H(1) and is donor in hydrogen bonding interactions with four of the five near neighbour oxygen atoms. While the interactions of H(1,*W*) with O(4) and O(7) [Fig. 5, Table 6(i)] constitute a symmetrical bifurcated hydrogen bond very similar to that described in the crystal structure of violuric acid monohydrate (Craven & Takei, 1964), the interactions of H(2,*W*) with O(2)′ and O(2)″ might be described either as an asymmetrical bifurcated hydrogen bond, or possibly better as one normal hydrogen bond H···O(2)′, 2·07 Å; and a short van der Waals interaction H···O(2)″, 2·47 Å.

Table 6. *Intermolecular distances and angles in 5-nitrouracil monohydrate*

Distances are not corrected for the effect of thermal motion and thus must be regarded as lower limits. E.s.d.'s in distances between heavier atoms are about 0·006 Å. E.s.d.'s in angles are listed individually.

Atoms not in the crystal chemical unit (as listed in Table 3) are specified by a subscript. The four-digit subscript denotes how the atomic parameters can be derived from the corresponding atom in the crystal chemical unit. The first three digits code a lattice translation, *e.g.* 564 means a translation of $(5-5)\mathbf{a}+(6-5)\mathbf{b}+(4-5)\mathbf{c}$ or $(\mathbf{b}-\mathbf{c})$. The fourth digit specifies one of the following operations;

(1) $x,\ y,\ z$
(2) $-x,\ -y,\ -z$
(3) $-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$
(4) $x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

(i) Hydrogen bonds (Hydrogen to acceptor atom distances are also shown in Fig. 5)

	d	Angle	*θ*, *σ*(*θ*)
N(1)····O(*W*)$_{5561}$	2·84 Å	N(1) H(1) O(*W*)$_{5561}$	148 (6)°
H(1)····O(*W*)$_{5561}$	2·11	H(1) O(*W*) H(1,*W*)	143 (5)
		H(1) O(*W*) H(2,*W*)	105 (6)
N(3)····O(4)$_{5562}$	2·85	N(3) H(3) O(4)$_{5562}$	170 (6)
H(3)····O(4)$_{5562}$	2·01	H(3) O(4)$_{5562}$ C(4)$_{5562}$	119 (2)
C(6)····O(7)$_{5554}$	3·25	C(6) H(6) O(7)$_{5554}$	171 (5)
H(6)····O(7)$_{5554}$	2·30	H(6) O(7)$_{5554}$ N(5)$_{5554}$	106 (2)
O(*W*)····O(7)	3·07	O(*W*) H(1,*W*) O(7)	154 (6)
H(1,*W*)····O(7)	2·30	H(1,*W*) O(7) N(5)	145 (2)
O(*W*)····O(4)	3·00	O(*W*) H(1,*W*) O(4)	135 (6)
H(1,*W*)····O(4)	2·35	O(4) H(1,*W*) O(7)	71 (2)
		H(1,*W*) O(4) C(4)	132 (2)
		H(1,*W*) O(4) O(7)	54 (2)
		H(1,*W*) O(7) O(4)	56 (2)
O(*W*)····O(2)$_{5562}$	2·94	O(*W*) H(2,*W*) O(2)$_{5562}$	171 (6)
H(2,*W*)····O(2)$_{5562}$	2·07	H(2,*W*) O(2)$_{5562}$ C(2)$_{5562}$	142 (2)

(ii) Other intermolecular interactions within a sheet such as is shown in Fig. 5.

Distance	*d*	Angle	*θ*, *σ*(*θ*)
N(1)····O(8)$_{5554}$	3·28 Å	N(1) H(1) O(8)$_{5554}$	131 (5)°
H(1)····O(8)$_{5554}$	2·68	H(1) O(8)$_{5554}$ N(5)$_{5554}$	130 (2)
O(*W*)····O(2)$_{5541}$	2·92	O(*W*) H(2,*W*) O(2)$_{5541}$	113 (5)
H(2, W)····O(2)$_{5541}$	2·47	H(2,*W*) O(2)$_{5541}$ C(2)$_{5541}$	112 (2)
O(2)····O(2)$_{5572}$	2·74	C(2) O(2) O(2)$_{5572}$	157·9 (0·5)

Table 6 (*cont.*)

(iii) Interatomic distances from a sheet such as is shown in Fig. 5, and adjacent sheets.

All distances are listed which are within 0·2 Å of the sum of Pauling's (1960) van der Waals radii (C 1·7 Å, N 1·5 Å, O 1·4 Å). These distances are denoted by (v). If there are no such distances from a given atom in the crystal chemical unit (see Table 3, Fig. 5) then the shortest interatomic distance is given. Column (*a*) lists distances to atoms in the sheet *below* (negative *x*), and column (*b*) lists distances to atoms in the sheet *above* (positive *x*) the sheet shown in Fig. 5.

(*a*)		(*b*)	
N(1)····C(4)$_{4551}$	3·50 Å	N(1)····O(*W*)$_{6561}$	3·30 Å
N(1)····O(4)$_{4551}$	3·31		
C(2)····O(4)$_{4551}$	3·16 (v)	C(2)····O(*W*)$_{6561}$	3·30 (v)
O(2)····C(4)$_{4551}$	3·59	O(2)····N(3)$_{7572}$	3·45
N(3)····O(*W*)$_{4551}$	3·44	N(3)····O(*W*)$_{6561}$	3·30
C(4)····O(*W*)$_{4551}$	3·07 (v)	C(4)····N(1)$_{6551}$	3·50
O(4)····C(2)$_{4541}$	3·58	O(4)····C(2)$_{6551}$	3·16 (v)
C(5)····O(*W*)$_{4551}$	3·25 (v)	C(5)····O(8)$_{6554}$	3·44
N(5)····O(8)$_{4544}$	3·26	N(5)····O(8)$_{6554}$	3·25
O(7)····N(1)$_{4541}$	3·48	O(7)····	<3·6
O(8)····O(8)$_{4544}$	3·15	O(8)····O(8)$_{6554}$	3·15
····C(6)$_{4544}$	3·45	····N(5)$_{6554}$	3·26
C(6)····	>3·6	C(6)····O(8)$_{6554}$	3·45
		····O(*W*)$_{6561}$	3·35
O(*W*)····C(2)$_{4541}$	3·30 (v)	O(*W*)····C(4)$_{6551}$	3·07 (v)
····N(1)$_{4541}$	3·30	····C(5)$_{6551}$	3·25 (v)
····N(3)$_{4541}$	3·30		

While the weak hydrogen bonds in this crystal structure have been categorized as 'bent', 'bifurcated', or even as van der Waals interactions, it cannot be inferred that these represent well defined bond types. The wide variety of hydrogen bonding angles and distances in the water molecule environment suggests that these are all the result of electrostatic interactions, *i.e.* that the water molecule orientation is determined by an electrostatic field dominated by the neighboring oxygen atom lone pair electrons and by the effective positive charge of the N(1)H(1) imine group. A similar point of view has been emphasized by Baur (1965) in reviewing the hydrogen bonding in crystalline hydrates.

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