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The Crystal and Molecular Structure of the *trans-syn* Photodimer of Methyl Orotate*

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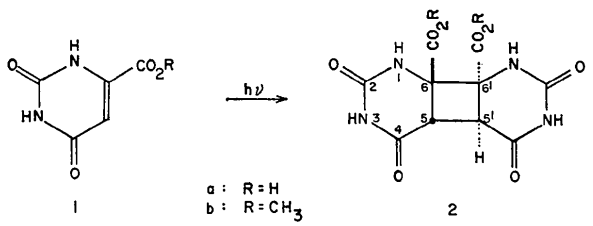
The photodimer of methyl orotate, formed upon ultraviolet irradiation of the monomer in aqueous solution, crystallizes as the dihydrate, $C_{12}H_{12}O_8N_4.2H_2O$. The crystals are monoclinic, space group $C2/c$ ($Z=4$), with $a=14{\cdot}024\pm0{\cdot}002$, $b=6{\cdot}722\pm0{\cdot}002$, $c=17{\cdot}006\pm0{\cdot}002$ Å, $\beta=105{\cdot}11\pm0{\cdot}02°$. Data were collected at room temperature with an automatic four-circle Picker diffractometer. The structure was determined by the symbolic addition method and refined by the least-squares procedure to a final value of $R=0{\cdot}042$. Two almost flat pyrimidine rings are fused to a slightly puckered (dihedral angle 169·5°) cyclobutane ring in the *trans–syn* configuration. The pyrimidine rings are twisted by 7° with respect to one another, and the lengths of the two interpyrimidine bonds are 1·556 (2) and 1·628 (2) Å. The high density of the crystals ($D_x=1{\cdot}61$, $D_m=1{\cdot}63$ g.cm^{-3}) is attributable to an extensive network of hydrogen bonds which includes a bifurcated bond.

Introduction

Photodimerization of pyrimidines is one of the reactions which contributes to mutagenic and lethal effects of ultraviolet irradiation of micro-organisms. Consequently, there has been great interest in the photochemistry of pyrimidines and in the structures of their photodimers. Some of the latter have been determined by X-ray crystallography and they include examples of three of the four possible cyclobutane isomers (Wulff & Fraenkel, 1961). The photochemistry and dimerization of orotic acid (1*a*) and its methyl ester (1*b*) have been studied extensively in recent years (Sztumpf & Shugar, 1965; Sztumpf-Kulikowska, Shugar & Boag, 1967; Herbert, Hunt & Johns, 1968; Yip, Riddell & Szabo, 1970), and it was suggested that the *trans-anti* dimer was obtained from irradiation of orotic acid in aqueous solution (Lisewski & Wierzchowski, 1970). In order to interpret recent mechanistic studies (Whillans & Johns, 1969; Charlier, Hélène & Dourlent, 1969; Yip *et al.*, 1970), a definite knowledge of the structure of the photoproduct was necessary and this led to the present X-ray analysis. Its results revealed that the structure of methyl orotate photodimer has the *trans-syn* configuration (2*b*). The photodimer of orotic acid was shown to have the same stereochemistry (2*a*), since upon methylation with diazomethane it yielded a product identical to that obtained from photodimerization of methyl orotate (Birnbaum, Dunston & Szabo, 1971).



1 2

This being the first crystal-structure analysis of a *trans-syn* pyrimidine cyclobutane dimer, it may be of interest to recall that the corresponding isomer of a thymine dimer was isolated from ultraviolet-irradiated denatured DNA (Ben-Hur & Ben-Ishai, 1968).

Experimental

Crystal data

Methyl orotate photodimer dihydrate,

$C_{12}H_{12}O_8N_4.2H_2O$; F.W. 376·2; monoclinic:

$a=14{\cdot}024\pm0{\cdot}002$ Å	$D_x=1{\cdot}61$ g.cm^{-3}
$b=6{\cdot}722\pm0{\cdot}002$	$D_m=1{\cdot}63$ g.cm^{-3} (flotation)
$c=17{\cdot}006\pm0{\cdot}002$	$Z=4$
$\beta=105{\cdot}11\pm0{\cdot}02°$	$F(000)=768$
$V=1547{\cdot}7$ Å^3	$\mu=12{\cdot}6$ cm^{-1} (Cu $K\alpha$)

Absent reflexions: $h0l$ when l is odd, hkl when $h+k$ is odd. Possible space groups: Cc or $C2/c$. Space group $C2/c$ determined from statistics of E's.

The material was obtained by ultraviolet irradiation of aqueous solutions of methyl orotate. The crystals were grown from a mixture of ethanol and water. They were colourless plates with a trapezoid face perpendicular to **c***. One of them was cut to a size of 0·2 × 0·4 × 0·5 mm and mounted along the *b* axis on an automated Picker four-circle diffractometer, equipped with a Cu target tube and a scintillation counter. The cell dimensions were measured at room temperature at a small take-off angle and a narrow slit, using both Cu $K\alpha_1$ ($\lambda=1{\cdot}5405$ Å) and Cu $K\alpha_2$ ($\lambda=1{\cdot}5443$ Å) radiations. Monochromatization was achieved by a nickel filter and a pulse-height analyser. The moving-crystal, moving-counter method ($\theta/2\theta$ scan) was used to measure the intensity data (2° scans for $2\theta<100°$, 3° for $2\theta\geq100°$) and background counts were recorded at the beginning and end of each scan. When the count rate exceeded 20000 cps the current was reduced and, where necessary, brass attenuators were used. Two standard reflexions (602 and 170) were monitored at

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intervals of 2 hours. Their average intensity decreased by 12% after 40% of the data had been measured, and the crystal was replaced by another one of similar dimensions and mounted in the same manner. The rest of the data were collected from the second crystal whose average intensity decreased by only 2%. A net count of 100 or 5% of the background, whichever was higher, was accepted as threshold intensity below which reflexions were considered unobserved. Of 1308 reflexions accessible to the diffractometer ($2\theta \leq 130°$), 1234 (94%) had intensities above threshold values. Absorption corrections were not applied. The minimum and maximum absorption correction factors (A^*) would be approximately 1·2 and 1·6, respectively.

Structure determination

A calculation of the statistical distribution of E values indicated a centrosymmetric space group, and the structure was solved by the symbolic-addition method (Karle & Karle, 1966). The first E map revealed the positions of all 13 nonhydrogen atoms, including that of the water oxygen atom.

The atomic scattering factors for C, N, and O were those given by Hanson, Herman, Lea & Skillman (1964) and those for bonded H were taken from Stewart, Davidson & Simpson (1965). The oxygen curve was corrected for anomalous dispersion with $\Delta f' = 0{\cdot}0$ and $\Delta f'' = 0{\cdot}1$ (*International Tables for X-ray Crystallography*, 1962).

After five cycles of least-squares refinement, using the block-diagonal approximation and isotropic temperature parameters, the value of R decreased to 13·2%. Throughout the refinement, the function $\sum w(|F_o| - |F_c|)^2$ was minimized and a factor of 0·8 was applied to all shifts. After three cycles with anisotropic temperature parameters, a low-angle difference Fourier map revealed the positions of the eight hydrogen atoms on peaks ranging in height from 0·50 to 0·82 e.Å^{-3}. These atoms were included in the subsequent refinement. The weighting scheme introduced at this stage was $w = w_1 \,.\, w_2$, where

$$\begin{aligned} w_1 &= 1 && \text{for } |F_o| \leq 18 \\ &= 18/|F_o| && \text{for } |F_o| > 18 \\ w_2 &= (\sin^2\theta + 0{\cdot}3)/2 && \text{for } \sin^2\theta \leq 0{\cdot}33 \\ &= 1 && \text{for } \sin^2\theta > 0{\cdot}33\,. \end{aligned}$$

This weighting scheme was fairly successful in eliminating the dependence of $w\Delta F^2$ on $|F_o|$ and $\sin^2\theta$. It was noted that the two strongest reflexions (002, $|F_c| = 189{\cdot}7$ and 402, $|F_c| = 310{\cdot}3$) were affected by extinction, while for two others (244 and $24\bar{4}$) $|F_o| \simeq 2{\cdot}5|F_c|$, possibly due to double reflexions. These four reflexions were excluded from the subsequent refinement.

The refinement converged after the 13th cycle, with the average coordinate shift equalling $0{\cdot}1\sigma$ and the largest one $0{\cdot}5\sigma$. The agreement index $R = (\sum|\Delta F|/\sum|F_o|)$ for 1230 observed reflexions was 0·042, and the weighted index $R' = (\sum w\Delta F^2/\sum wF_o^2)^{1/2}$ was 0·050. A final difference Fourier map showed four minima ($-0{\cdot}30$ to $-0{\cdot}35$ e.Å^{-3}) in the plane of the pyrimidine ring: three of them at the periphery and the fourth in the centre of the ring. Such minima, which are due to bonding effects, have been observed in the past and were recently discussed by Verschoor & Keulen (1971). There was also a positive peak of 0·24 e.Å^{-3}, which can be ascribed to a disordered hydrogen atom (see below). The final coordinates and temperature parameters for non-hydrogen atoms are listed in Table 1 and those for hydrogen atoms are given in Table 2. The esti-

Table 2. *Final parameters (and their e.s.d.'s) of the hydrogen atoms*

All values are ×10³. H(W2*) refers to the minor position of the disordered atom

	x/a	y/b	z/c	U_{iso}
H(11)	121 (2)	581 (4)	232 (2)	37 (6) Å^2
H(31)	189 (2)	95 (4)	138 (2)	40 (6)
H(51)	84 (2)	48 (3)	315 (1)	23 (4)
H(81)	145 (3)	607 (5)	486 (2)	65 (9)
H(82)	42 (3)	707 (7)	454 (3)	85 (11)
H(83)	135 (3)	814 (7)	444 (3)	80 (11)
H(W1)	196 (3)	755 (7)	95 (3)	81 (11)
H(W2)	176 (5)	799 (11)	21 (4)	143 (21)
H(W2*)	227	783	29	

Table 1. *Final parameters (and their e.s.d.'s) of the nonhydrogen atoms*

All values are ×10⁴. The U^{ij} values are in Å^2 and are defined by
$\exp[-2\pi^2(U^{11}h^2a^{*2} + U^{22}k^2b^{*2} + U^{33}l^2c^{*2} + 2U^{23}klb^*c^* + 2U^{13}hla^*c^* + 2U^{12}hka^*b^*)]$.

	x/a	y/b	z/c	U^{11}	U^{22}	U^{33}	$2U^{23}$	$2U^{13}$	$2U^{12}$
N(1)	1233 (1)	4415 (2)	2331 (1)	289 (7)	191 (6)	331 (7)	−8 (10)	257 (11)	−24 (10)
C(2)	1696 (1)	3566 (2)	1813 (1)	242 (7)	232 (7)	290 (8)	52 (12)	167 (11)	12 (12)
O(2)	2179 (1)	4516 (2)	1441 (1)	424 (7)	320 (6)	437 (7)	68 (11)	497 (11)	−43 (10)
N(3)	1625 (1)	1510 (2)	1727 (1)	348 (7)	238 (7)	380 (7)	−11 (12)	381 (11)	97 (11)
C(4)	1089 (1)	257 (2)	2069 (1)	298 (7)	201 (7)	388 (8)	31 (13)	230 (14)	111 (12)
O(4)	1035 (1)	−1505 (2)	1912 (1)	606 (8)	174 (6)	684 (10)	−79 (11)	704 (15)	44 (11)
C(5)	573 (1)	1128 (2)	2660 (1)	281 (8)	169 (7)	314 (8)	78 (12)	216 (12)	28 (12)
C(6)	588 (1)	3420 (2)	2727 (1)	238 (8)	177 (7)	270 (7)	19 (11)	170 (12)	−2 (11)
C(7)	709 (1)	4129 (2)	3598 (1)	237 (7)	280 (8)	287 (8)	10 (12)	140 (11)	−22 (12)
O(7)	518 (1)	3102 (2)	4112 (1)	496 (7)	472 (7)	299 (6)	35 (11)	280 (10)	−232 (12)
O(8)	974 (1)	6016 (2)	3679 (1)	516 (7)	279 (6)	302 (6)	−117 (10)	207 (10)	−77 (11)
C(8)	1045 (1)	6909 (4)	4468 (1)	784 (16)	471 (12)	337 (9)	−276 (19)	226 (19)	−45 (22)
O(W)	2108 (1)	8493 (3)	634 (1)	702 (10)	549 (9)	632 (10)	−80 (16)	753 (17)	−127 (16)

mated standard deviations (shown in parentheses and referring always to the last digits) were derived from the inverse of the least-squares matrix. Observed and calculated structure factors are shown in Table 3.

The structure was subjected to a rigid-body analysis in terms of translation (**T**), libration (**L**), and screw motion (**S**) tensors (Schomaker & Trueblood, 1968), both with and without the $-CO_2CH_3$ groups in the assumed rigid body. The centre of the cyclobutane ring was taken as the centre of gravity. In each case, the value of $\sigma(U_{\text{calc}})=[\sum(\Delta U^{ij})^2/(n-s)]^{1/2}$ was several times higher than the average value of $\sigma(U^{ij}_{\text{obs}})$, indicating that the assumption of a rigid body was not justified. The 12 hydrogen bonds connecting each dimer molecule to other molecules (see below) may preclude rigid-body vibration. Consequently, no corrections were applied to bond lengths and angles.

Discussion of the structure

The structure revealed by this X-ray analysis is that of a *trans-syn* cyclobutane dimer (Fig. 1). The asymmetric unit consists of one-half of the molecule, the two halves being related by an axis of twofold rotation

Table 3. *Observed and calculated structure factors* (×10)

An asterisk indicates an unobserved reflexion to which the estimated threshold value was assigned.

K	|FO|	FC
H= 0, L= 0		
2	97	84
4	1062	-1124
6	261	280
H= 0, L= 1		
2	821	812
4	175	-174
6	129	144
H= 0, L= 2		
0	1642	-1857
2	886	-950
4	512	422
6	88	-72
H= 0, L= 3		
2	158	151
4	55	-44
6	51	35
H= 0, L= 4		
0	453	-450
2	70	-48
4	110	90
6	142	156
H= 0, L= 5		
2	309	265
4	276	-260
6	101	-98
H= 0, L= 6		
0	143	-144
2	398	387
4	174	-165
6	41	42
H= 0, L= 7		
2	68	70
4	117	110
6	302	-322
H= 0, L= 8		
0	275	-288
2	719	703
4	74	72
6	508	-503
H= 0, L= 9		
2	457	-444
4	455	508
6	317	309
H= 0, L= 10		
0	454	-448
2	223	-230
4	161	155
6	219	214
H= 0, L= 11		
2	115	-114
4	231	-236
6	133	-135
H= 0, L= 12		
0	28	-25
2	253	-248
4	59	-48
6	86	80
H= 0, L= 13		
2	32	34
4	52	-50
H= 0, L= 14		
0	226	241
2	220	210
4	55	82
H= 0, L= 15		
2	135	152
4	40	-28
H= 0, L= 16		
0	105	100
2	20*	-14
4	149	-142
H= 0, L= 17		
2	67	56
H= 0, L= 18		
0	83	-76
2	108	-100
H= 1, L= 0		
1	691	-680
3	285	294
5	38	19
7	281	292
H= 1, L= 1		
1	755	-755
3	766	-751
5	298	-303
7	130	-146
1	829	773
3	201	195
5	65	-70
7	68	75
H= 1, L= 2		
1	725	-713
3	1149	1055
5	90	-85
7	186	-195
1	223	225
3	613	-581
5	137	-138
7	35	23
H= 1, L= 3		
1	1027	1040
3	1077	1030
5	80	86
7	47	58
1	27	5
3	47	20
5	64	65
7	109	114
H= 1, L= 4		
1	288	288
3	15*	6
5	240	-247
7	35	40
1	945	904
3	239	-253
5	195	-202
7	172	-168
H= 1, L= 5		
1	378	-364
3	277	-275
5	31	33
7	36	-29
1	195	-215
3	282	266
5	21	-23
7	142	-145
H= 1, L= 6		
1	89	-51
3	200	-224
5	38	40
7	88	-90
1	499	488
3	477	-473
5	611	611
7	132	137
H= 1, L= 7		
1	17	-7
3	256	-268
5	103	103
7	68	60
1	1224	-1172
3	273	-279
5	296	293
7	69	-68
H= 1, L= 8		
1	536	-540
3	156	155
5	305	312
7	16	5
1	708	-712
3	132	-117
5	33	-35
7	70	-64
H= 1, L= 9		
1	282	292
3	281	-278
5	203	-201
1	101	110
3	39	54
5	170	-166
7	24	-23
H= 1, L= 10		
1	436	458
3	20*	3
5	45	39
1	199	190
3	201	198
5	84	-86
H= 1, L= 11		
1	198	172
3	232	226
5	185	186
1	108	-99
3	76	-71
5	342	345
H= 1, L= 12		
1	47	-48
3	292	-301
5	213	-201
1	176	169
3	165	171
5	189	-189
H= 1, L= 13		
1	198	-190
3	21*	-13
5	21	-17
1	429	430
3	91	-83
5	311	-299
H= 1, L= 14		
1	71	72
3	129	133
5	53	57
1	357	-376
3	73	85
5	175	170
H= 1, L= 15		
1	168	-175
3	20*	-17
1	248	267
3	21*	19
5	86	-84
H= 1, L= 16		
1	82	-78
3	127	-116
1	87	93
3	79	-77
H= 1, L= 17		
1	19*	-7
3	69	69
1	186	-184
3	23	-24
H= 1, L= 18		
1	113	102
1	51	42
3	37	-37
H= 1, L=-19		
1	27	25
H= 2, L= 0		
0	354	356
2	335	-310
4	162	-135
6	55	-49
H= 2, L= 1		
2	445	427
4	377	-380
6	91	-68
2	713	681
4	434	411
6	66	-73
H= 2, L= 2		
0	712	-695
2	187	-200
4	298	290
6	315	-340
0	421	-407
2	149	121
4	253	248
6	287	292
H= 2, L= 3		
2	449	-437
4	112	-107
6	140	149
2	52	-37
4	229	-205
6	127	131
H= 2, L= 4		
0	1807	1939
2	54	48
4	253	-97
6	348	376
0	1258	-1235
2	476	444
4	194	68
6	220	-225
H= 2, L= 5		
2	115	110
4	35	-26
6	92	97
2	532	524
4	349	-346
6	238	-242
H= 2, L= 6		
0	1585	-1597
2	280	-295
4	329	295
6	71	-45
0	304	306
2	519	488
4	239	-236
6	136	-130
H= 2, L= 7		
2	191	-215
4	226	224
6	24	-19
2	23	-33
4	85	-78
6	174	175
H= 2, L= 8		
0	401	392
2	276	272
4	200	-193
6	137	-133
0	397	398
2	558	-531
4	511	-525
6	160	162
H= 2, L= 9		
2	213	-213
4	244	252
6	132	-121
2	222	195
4	308	309
6	24	15
H= 2, L= 10		
0	676	683
2	129	-126
4	391	-399
6	183	183
0	257	-242
2	243	225
4	672	681
6	19*	-10
H= 2, L= 11		
2	102	-102
4	85	-80
6	106	-99
2	399	-402
4	98	-91
6	107	-108
H= 2, L= 12		
0	382	-391
2	126	129
4	340	349
0	334	339
2	300	-292
4	258	-271
6	96	95
H= 2, L= 13		
2	21*	9
4	170	158
2	362	-370
4	336	342
H= 2, L= 14		
0	32	30
2	148	-148
4	113	-118
0	21*	13
2	55	51
4	41	-49
H= 2, L= 15		
2	228	217
4	301	-289
2	21*	24
4	112	-106
H= 2, L= 16		
0	20*	-26
2	122	113
0	251	-254
2	80	93
4	182	181
H= 2, L= 17		
2	101	98
2	272	275
4	48	43
H= 2, L= 18		
0	84	-78
0	19*	-5
2	43	-40
H= 2, L=-19		
2	96	-96
H= 3, L= 0		
1	63	57
3	698	661
5	250	-243
7	195	-189
H= 3, L= 1		
1	146	-151
3	295	300
5	264	262
7	180	187
1	114	-122
3	287	-258
5	80	-84
7	85	-85
H= 3, L= 2		
1	1548	-1553
3	283	289
5	182	173
7	154	144
1	1080	1047
3	374	-331
5	85	89
7	50	42
H= 3, L= 3		
1	1254	-1225
3	192	-198
5	133	130
7	168	-170
1	250	-218
3	118	-123
5	213	209
7	19*	9
H= 3, L= 4		
1	629	645
3	242	-227
5	175	-130
7	161	161
1	595	-544
3	33	-41
5	31	33
7	292	-287
H= 3, L= 5		
1	401	-401
3	73	74
5	63	-60
7	173	-176
1	1263	1210
3	262	267
5	772	-779
7	51	-47
H= 3, L= 6		
1	435	437
3	40	18
5	267	-289
7	162	-170
1	579	-555
3	305	-292
5	560	555
7	270	261
H= 3, L= 7		
1	206	222
3	201	193
5	143	152
7	123	126
1	597	-574
3	124	118
5	660	680
7	176	161
H= 3, L= 8		
1	107	100
3	186	-190
5	234	242
1	929	896
3	101	98
5	379	-376
7	126	-127
H= 3, L= 9		
1	310	330
3	250	-237
5	168	-168
1	378	354
3	181	-148
5	466	-454
7	115	-109
H= 3, L= 10		
1	336	-337
3	84	-75
5	20*	7
1	59	-56
3	83	-75
5	158	-153
H= 3, L= 11		
1	183	185
3	113	-121
5	20*	-14
1	301	301
3	51	-45
5	54	-60
H= 3, L= 12		
1	57	47
3	173	179
5	31	-25
1	43	-53
3	59	58
5	53	-42
H= 3, L= 13		
1	302	308
3	123	139
5	195	-192
1	47	-51
3	21*	5
5	211	201
H= 3, L= 14		
1	167	169
3	105	96
1	277	-276
3	21*	-9
5	166	164
H= 3, L= 15		
1	260	-254
3	19*	1
1	88	-78
3	21*	-12
5	17*	-8
H= 3, L= 16		
1	220	-210
3	161	-154
1	393	397
3	45	27
H= 3, L= 17		
1	95	-83
1	136	-138
3	19*	13
H= 3, L=-18		
1	182	-186
3	32	-26
H= 3, L=-19		
1	193	-179
H= 4, L= 0		
0	1496	-1589
2	205	-200
4	367	298
6	59	-49
H= 4, L= 1		
2	309	-281
4	111	106
6	23	-16
2	508	-495
4	24	-18
6	182	-184
H= 4, L= 2		
0	2685	3103
2	195	212
4	631	-549
6	94	82
0	1236	-1252
2	444	450
4	334	268
6	89	99
H= 4, L= 3		
2	604	632
4	180	172
6	189	196
2	1058	-968
4	226	217
6	182	179
H= 4, L= 4		
0	345	-371
2	581	-505
4	53	-38
6	37	27
0	560	-529
2	44	51
4	527	-519
6	134	-121
H= 4, L= 5		
2	110	102
4	543	-551
6	21*	-26
2	606	549
4	302	301
6	93	103
H= 4, L= 6		
0	386	-386
2	78	-73
4	178	180
6	22	14
0	256	-229
2	579	913
4	562	559
6	412	-410
H= 4, L= 7		
2	154	156
4	205	-208
6	71	81
2	275	251
4	536	-537
6	229	-224
H= 4, L= 8		
0	210	198
2	184	184
4	43	57
6	125	124
0	104	113
2	650	-601
4	25	-14
6	322	321
H= 4, L= 9		
2	168	160
4	163	167
6	190	-196
2	207	-204
4	255	253
6	41	36
H= 4, L= 10		
0	27	-17
2	43	41
4	142	-145
6	211	-211
0	188	-191
2	445	-443
4	89	88
6	77	68
H= 4, L= 11		
2	87	-58
4	256	244
2	138	147
4	108	-113
6	19	-23
H= 4, L= 12		
0	202	-196
2	44	-50
4	162	160
0	825	852
2	178	173
4	206	-198
6	17	-19
H= 4, L= 13		
2	262	-267
4	19*	-6
2	22	24
4	225	217
H= 4, L= 14		
0	215	228
2	134	-122
4	107	-105
0	80	-79
2	80	75
4	47	-43
H= 4, L= 15		
2	19*	-8
2	150	-144
4	199	-194
H= 4, L= 16		
0	192	-179
2	122	109
0	124	-125
2	74	-67
4	38	-34
H= 4, L=-17		
2	152	158
4	38	-34
H= 4, L=-18		
0	235	-227
2	18*	6
H= 4, L=-19		
2	16*	-9
H= 5, L= 0		
1	157	175
3	440	-433
5	201	-210
7	195	-195
H= 5, L= 1		
1	294	274
3	67	-44
5	114	106
7	85	93
1	1156	1123
3	144	152
5	511	-506
7	18*	-5
H= 5, L= 2		
1	368	253
3	70	21
5	120	115
7	196	199
1	527	538
3	673	-677
5	185	177
7	119	121
H= 5, L= 3		
1	536	-536
3	479	-453
5	66	-65
7	53	-57
1	602	-579
3	100	94
5	575	562
7	80	68
H= 5, L= 4		
1	230	-240
3	313	330
5	54	57
7	52	-44
1	230	205
3	17*	-4
5	304	301
7	34	-27
H= 5, L= 5		
1	549	546
3	735	753
5	106	-115
7	41	43
1	565	-525
3	300	-271
5	84	-74
7	47	-44
H= 5, L= 6		
1	335	-355
3	92	91
5	162	-164
1	490	-486
3	145	144
5	34	-26
7	17*	-4
H= 5, L= 7		
1	613	-648
3	85	-98
5	172	176
1	85	-66
3	87	-94
5	158	-160
7	33	-32
H= 5, L= 8		
1	434	453
3	160	-163
5	21*	13
1	90	90
3	278	257
5	423	-415
7	40	47
H= 5, L= 9		
1	66	58
3	21*	13
5	55	-53
1	29	14
3	231	234
5	349	368
H= 5, L= 10		
1	307	-317
3	159	158
5	19*	8
1	358	-371
3	374	382
5	21*	-20
H= 5, L= 11		
1	21*	-1
3	204	-204
5	30	26
1	273	278
3	90	-99
5	240	-238
H= 5, L= 12		
1	28	31
3	116	109
5	106	103
1	89	-75
3	171	180
5	149	159
H= 5, L= 13		
1	188	193
3	80	79
1	267	274
3	93	93
5	211	-204
H= 5, L= 14		
1	20*	-5
3	116	-113
1	77	78
3	301	-303
5	31	27
H= 5, L= 15		
1	49	-39
3	43	-42
1	439	-438
3	105	-114
5	222	219
H= 5, L= 16		
1	44	41
1	98	102
3	102	-104
H= 5, L=-17		
1	211	206
3	278	279
H= 5, L=-18		
1	143	138
3	17*	-10
H= 5, L=-19		
1	202	-194
H= 6, L= 0		
0	1136	-1050
2	227	-239
4	139	76
6	113	112
H= 6, L= 1		
2	284	-293
4	332	336
6	44	-42
2	111	111
4	35	-32
6	27	26
H= 6, L= 2		
0	213	200
2	36	41
4	54	-49
6	64	69
0	307	325
2	502	490
4	37	-15
6	112	-117
H= 6, L= 3		
2	244	244
4	245	-259
6	178	-179
2	231	204
4	56	-45
6	129	-119
H= 6, L= 4		
0	428	-436
2	120	120
4	167	177
6	298	-306
0	1026	1041
2	196	185
4	312	-293
6	90	-90
H= 6, L= 5		
2	127	124
4	65	61
6	87	87
2	273	-252
4	29	-28
6	37	28
H= 6, L= 6		
0	762	785
2	97	103
4	167	-162
6	137	137
0	319	-272
2	888	-832
4	134	-139
6	192	184
H= 6, L= 7		
2	33	-32
4	150	-149
6	232	228
2	266	226
4	49	-49
6	91	82
H= 6, L= 8		
0	974	-999
2	165	-168
4	293	296
6	27	4
0	678	665
2	51	38
4	296	287
6	195	193
H= 6, L= 9		
2	119	-116
4	101	-104
2	512	-490
4	210	218
6	77	74
H= 6, L= 10		
0	318	322
2	53	55
4	159	-161
0	81	-65
2	19*	-17
4	57	-58
6	148	-140
H= 6, L= 11		
2	86	92
4	120	111
2	145	-151
4	21*	5
6	38	-35
H= 6, L= 12		
0	261	262
2	25	-21
4	49	-40
0	219	216
2	155	162
4	155	-209
6	37	-42
H= 6, L= 13		
2	61	-57
4	70	61
2	151	154
4	108	-95
H= 6, L= 14		
0	39	21
2	92	-84
0	521	-551
2	47	42
4	313	312
H= 6, L= 15		
2	56	-92
2	211	216
4	19*	10
H= 6, L= 16		
0	57	-52
0	154	157
2	111	116
4	78	-77
H= 6, L=-17		
2	20*	-11
H= 6, L=-18		
0	131	130
2	19	-23
H= 6, L=-19		
2	80	74
H= 7, L= 0		
1	262	268
3	28	-26
5	71	77
7	57	-58
H= 7, L= 1		
1	345	352
3	135	128
5	162	162
7	16*	-14
1	160	173
3	64	-73
5	37	15
7	41	45
H= 7, L= 2		
1	215	214
3	90	56
5	169	-176
1	234	-233
3	199	191
5	59	61
7	175	-171
H= 7, L= 3		
1	147	166
3	106	-116
5	55	-51
1	452	466
3	135	-120
5	685	-705
7	43	-42
H= 7, L= 4		
1	759	-775
3	55	52
5	179	184
1	464	-445
3	257	-260
5	205	207
7	310	308
H= 7, L= 5		
1	319	-323
3	181	-163
5	29	-26
1	620	-612
3	258	241
5	701	707
7	124	116
H= 7, L= 6		
1	352	364
3	36	40
5	25	-18
1	446	394
3	180	175
5	422	-410
H= 7, L= 7		
1	403	-407
3	28	20
5	155	160
1	257	257
3	73	81
5	339	-344
H= 7, L= 8		
1	168	174
3	150	-201
5	21	-20
1	249	250
3	81	79
5	57	-56
H= 7, L= 9		
1	289	302
3	269	360
5	67	-68
1	159	153
3	20*	-11
5	73	-77
H= 7, L= 10		
1	59	-59
3	61	-57
5	16*	6
1	213	-221
3	134	-128
5	95	91
H= 7, L= 11		
1	237	-243
3	280	-271
1	558	-553
3	122	-119
5	310	302
H= 7, L= 12		
1	21*	-8
3	32	-24
1	280	-280
3	69	-63
5	127	133
H= 7, L= 13		
1	173	172
3	20	-10
1	284	279
3	276	258
5	75	-74
H= 7, L= 14		
1	43	-48
1	576	595
3	96	-110
5	30	11
H= 7, L= 15		
1	125	119
1	264	-274
3	101	-102
H= 7, L=-16		
1	256	-261
3	63	69
H= 7, L=-17		
1	20*	-2
3	19	-17
H= 7, L=-18		
1	147	-139
3	68	72
H= 7, L=-19		
1	133	135
H= 8, L= 0		
0	468	-450
2	374	359
4	328	375
6	76	-76
H= 8, L= 1		
2	539	-545
4	247	257
6	45	-40
2	465	-459
4	58	-56
6	40	28
H= 8, L= 2		
0	33	28
2	108	-106
4	35	-26
6	149	150
0	171	-164
2	345	-320
4	473	-469
6	45	-42
H= 8, L= 3		
2	69	-61
4	41	-34
6	61	-55
2	813	801
4	150	154
6	20*	-2
H= 8, L= 4		
0	332	354
2	37	-34
4	90	-90
6	54	-48
0	167	167
2	456	411
4	425	420
6	109	-103
H= 8, L= 5		
2	156	198
4	357	362
6	19	21
2	23	16
4	296	-293
6	94	90
H= 8, L= 6		
0	247	248
2	111	-108
4	154	-161
0	232	-216
2	359	-318
4	116	115
6	59	97
H= 8, L= 7		
2	73	-65
4	364	-361
2	63	57
4	151	-150
6	71	-71
H= 8, L= 8		
0	297	-316
2	64	68
4	144	139
0	409	386
2	186	-183
4	161	-159
6	125	128
H= 8, L= 9		
2	119	126
4	64	-54
2	170	181
4	67	-69
6	65	-68
H= 8, L= 10		
0	89	84
2	96	100
4	39	-36
0	82	89
2	113	90
4	175	-173
6	86	-84
H= 8, L= 11		
2	42	37
4	27	-23
2	66	78
4	276	293
H= 8, L= 12		
0	184	-186
2	19*	3
0	83	-88
2	206	214
4	21*	5
H= 8, L= 13		
2	74	63
2	185	-185
4	160	-165
H= 8, L= 14		
0	81	84
0	121	-109
2	21*	1
4	64	56
H= 8, L=-15		
2	31	-26
4	58	-50
H= 8, L=-16		
0	143	-146
2	113	-114
4	43	-40
H= 8, L=-17		
2	19*	-17
H= 8, L=-18		
0	195	195
2	89	90
H= 9, L= 0		
1	52	-52
3	309	-324
5	214	220
H= 9, L= 1		
1	633	623
3	68	72
5	549	-540
1	782	-790
3	115	-122
5	617	621
H= 9, L= 2		
1	241	251
3	27	-29
5	242	-247
1	142	-141
3	166	162
5	37	-33
H= 9, L= 3		
1	135	134
3	21*	-20
5	181	184
1	96	-110
3	52	53
5	219	-217
H= 9, L= 4		
1	20*	16
3	21*	14
5	87	83
1	149	141
3	110	107
5	68	60
H= 9, L= 5		
1	33	-29
3	176	-175
5	23	-16
1	262	-263
3	20*	4
5	58	55
H= 9, L= 6		
1	21*	-10
3	91	100
5	33	-31
1	52	-59
3	186	179
5	352	-351
H= 9, L= 7		
1	116	122
3	76	82
5	100	-96
1	35	-30
3	49	49
5	160	162
H= 9, L= 8		
1	240	-259
3	37	-40
1	486	-484
3	159	164
5	161	161
H= 9, L= 9		
1	90	-97
3	82	74
1	384	372
3	27	-20
5	188	-186
H= 9, L= 10		
1	339	342
3	53	-55
1	278	285
3	74	-70
5	184	172
H= 9, L= 11		
1	51	-53
3	42	34
1	153	158
3	23	27
5	41	-39
H= 9, L= 12		
1	155	-153
1	116	116
3	185	-190
5	72	-65
H= 9, L= 13		
1	16*	3
1	127	-146
3	67	-108
5	35	-32
H= 9, L=-14		
1	82	86
3	200	-196
H= 9, L=-15		
1	113	122
3	200	208
H= 9, L=-16		
1	20*	-2
3	49	47
H= 9, L=-17		
1	89	-91
3	133	-134
H= 9, L=-18		
1	113	-103
H= 10, L= 0		
0	106	101
2	279	244
4	123	124
6	27	-30
H= 10, L= 1		
2	172	174
4	45	47
6	48	-51
2	172	168
4	33	38
6	153	154
H= 10, L= 2		
0	169	-156
2	321	-328
4	247	-248
0	444	436
2	103	112
4	167	-166
6	137	-132
H= 10, L= 3		
2	261	-267
4	87	-91
2	36	35
4	182	-179
6	108	-111
H= 10, L= 4		
0	74	-80
2	126	122
4	242	245
0	254	-262
2	370	-360
4	55	51
6	195	192
H= 10, L= 5		
2	21*	-2
4	115	118
2	88	-91
4	219	-222
6	129	120
H= 10, L= 6		
0	170	178
2	25	-26
4	84	-79
0	222	216
2	39	-33
4	21*	-8
6	78	81
H= 10, L= 7		
2	155	159
4	39	35
2	211	-210
4	385	384
6	83	85
H= 10, L= 8		
0	66	73
2	23	-15
4	43	-41
0	365	-379
2	174	175
4	116	117
H= 10, L= 9		
2	28	-23
2	58	68
4	38	-5
H= 10, L= 10		
0	328	-315
2	18*	21
0	407	407
2	226	229
4	171	-161
H= 10, L= 11		
2	201	-198
2	112	-116
4	79	-65
H= 10, L= 12		
0	66	61
0	1008	-1049
2	141	-142
4	253	262
H= 10, L=-13		
2	96	96
4	36	28
H= 10, L=-14		
0	312	318
2	118	115
4	26	-7
H= 10, L=-15		
2	167	157
H= 10, L=-16		
0	456	446
2	106	-106
H= 10, L=-17		
2	33	-32
H= 10, L=-18		
0	112	-110
H= 11, L= 0		
1	136	132
3	118	69
5	182	185
H= 11, L= 1		
1	178	187
3	104	115
5	131	-131
1	240	-244
3	238	-239
5	196	-191
H= 11, L= 2		
1	58	-58
3	21*	9
5	91	-96
1	181	-176
3	89	-88
5	73	-68
H= 11, L= 3		
1	27	-15
3	77	79
5	239	241
1	68	-61
3	274	276
5	237	232
H= 11, L= 4		
1	21*	29
3	78	68
5	32	-25
1	101	97
3	101	-103
5	87	-85
H= 11, L= 5		
1	164	179
3	34	-26
1	67	66
3	24	17
5	66	-60
H= 11, L= 6		
1	167	-178
3	67	62
1	269	273
3	37	38
5	19	-14
H= 11, L= 7		
1	111	-115
3	153	-151
1	211	210
3	21	14
5	31	-28
H= 11, L= 8		
1	57	59
3	81	74
1	158	-155
3	28	-35
5	123	122
H= 11, L= 9		
1	123	-113
1	392	-357
3	446	-464
5	74	68
H= 11, L= 10		
1	77	81
1	96	-96
3	156	-151
5	34	38
H= 11, L=-11		
1	344	349
3	388	401
5	16	6
H= 11, L=-12		
1	242	249
3	30	-12
H= 11, L=-13		
1	175	-183
3	75	-79
H= 11, L=-14		
1	176	-175
3	199	207
H= 11, L=-15		
1	54	-45
3	47	-50
H= 11, L=-16		
1	98	-101
H= 11, L=-17		
1	107	104
H= 12, L= 0		
0	133	-143
2	118	-117
4	141	-139
H= 12, L= 1		
2	49	49
4	86	-86
2	275	288
4	57	-52
H= 12, L= 2		
0	98	-93
2	195	190
4	100	98
0	83	93
2	140	131
4	96	85
H= 12, L= 3		
2	217	-226
4	132	130
2	92	-89
4	28	-26
H= 12, L= 4		
0	21*	-3
2	44	-37
4	57	51
0	492	-480
2	94	-91
4	226	222
H= 12, L= 5		
2	58	-56
4	85	-87
2	120	117
4	145	-149
H= 12, L= 6		
0	104	114
2	114	-114
0	857	848
2	33	37
4	325	-322
H= 12, L= 7		
2	89	92
2	63	-62
4	150	146
H= 12, L= 8		
0	135	121
2	29	-12
0	562	-567
2	80	-65
4	65	69
H= 12, L= -9		
2	21*	-6
4	110	108
H= 12, L=-10		
0	207	210
2	94	102
4	55	-55
H= 12, L=-11		
2	112	-115
4	17*	-17
H= 12, L=-12		
0	60	59
2	25	-24
4	55	59
H= 12, L=-13		
2	108	-106
H= 12, L=-14		
0	91	-86
2	76	-77
H= 12, L=-15		
2	120	110
H= 12, L=-16		
0	98	103
2	16*	-7
H= 13, L= 0		
1	78	-79
3	80	-74
H= 13, L= 1		
1	278	-278
3	56	-57
1	99	-103
3	20*	5
H= 13, L= 2		
1	61	-59
3	106	-105
1	142	141
3	76	80
H= 13, L= 3		
1	110	107
3	22	-25
1	142	146
3	203	198
H= 13, L= 4		
1	175	169
3	59	61
1	62	-62
3	104	96
H= 13, L= 5		
1	62	68
3	103	107
1	129	-123
3	248	-246
H= 13, L= 6		
1	76	-79
1	188	-182
3	38	28
H= 13, L= 7		
1	16*	-1
1	324	323
3	56	58
H= 13, L= -8		
1	40	43
3	70	-74
H= 13, L= -9		
1	31	33
3	39	31
H= 13, L=-10		
1	158	163
3	21	23
H= 13, L=-11		
1	20*	11
3	38	26
H= 13, L=-12		
1	49	44
3	150	-150
H= 13, L=-13		
1	164	-159
3	16*	-5
H= 13, L=-14		
1	137	-146
H= 13, L=-15		
1	17*	16
H= 14, L= 0		
0	32	-24
2	31	32
H= 14, L= 1		
2	117	120
2	20*	3
H= 14, L= 2		
0	92	-72
2	114	116
0	256	245
2	54	-53
4	48	-46
H= 14, L= 3		
2	49	48
2	203	-190
4	29	-33
H= 14, L= 4		
0	57	40
2	129	-130
0	251	-250
2	83	-79
4	73	77
H= 14, L= -5		
2	20*	-11
4	147	159
H= 14, L= -6		
0	28	24
2	30	35
4	33	-36
H= 14, L= -7		
2	91	100
4	163	158
H= 14, L= -8		
0	219	205
2	171	165
H= 14, L= -9		
2	181	-180
H= 14, L=-10		
0	455	-477
2	137	-134
H= 14, L=-11		
2	135	129
H= 14, L=-12		
0	132	140
2	59	46
H= 14, L=-13		
2	162	163
H= 14, L=-14		
0	381	380
H= 15, L= 0		
1	80	-85
H= 15, L= 1		
1	93	-95
1	51	41
H= 15, L= 2		
1	106	110
1	67	70
3	70	-67
H= 15, L= -3		
1	29	27
3	25	-18
H= 15, L= -4		
1	27	-22
3	49	50
H= 15, L= -5		
1	93	88
3	20	-14
H= 15, L= -6		
1	32	14
3	71	63
H= 15, L= -7		
1	139	-136
3	193	-203
H= 15, L= -8		
1	19	-14
H= 15, L= -9		
1	21	32
H= 15, L=-10		
1	26	-27
H= 15, L=-11		
1	34	30
H= 15, L=-12		
1	27	-26

which bisects the two interpyrimidine bonds. As usual the pyrimidine ring is not planar. The alternating signs and low values of the torsional angles (Fig. 2) indicate that its conformation is that of a very flat chair. Five atoms are within 0·023 Å of a mean plane, while C(6) is at a distance of 0·110 Å from it. Thus, the pyrimidine ring is flatter in this structure than in other photodimers which incorporate a puckered cyclobutane ring (Table 4). The small degree of this puckering is a predictable corollary. Another is the small extent of the relative twist between the two pyrimidine rings. This was taken as the average deviation of two torsional angles, C(4)–C(5)–C(5′)–C(4′) and N(1)–C(6)–C(6′)–N(1′), from the undistorted value of 120°. This conformation is believed to be connected with hydrogen bonding, which is discussed later. One of its consequences is the small torsional angle C(7)–C(6)–C(6′)–N(1′) (12·8°), indicating that the C(6)–C(7) and C(6′)–N(1′) bonds are almost eclipsed. The distance between N(1′) and C(7) is therefore so short (2·774 Å) that the latter atom is pushed out of the ester plane. The conformation of the ester group can be seen from the Newman projections in Fig. 3.

Most bond lengths and angles (Fig. 2) are in very good agreement with those in other pyrimidine photodimers (Table 4). The somewhat short C(7)–O(7) double bond is undoubtedly due to the thermal vibration of the latter atom. The most remarkable bond is C(6)–C(6′), which may be the longest in this class of compounds. The lengthening is due to the full substitution of these carbon atoms and to the repulsion resulting from the close distances between N(1′) and C(7) and between N(1) and C(7′). This weak bond accounts for the ease with which the photodimer splits into monomers by the action of radiation and/or elevated temperature (Birnbaum *et al.*, 1971). On the other hand, the relatively strong C(5)–C(5′) bond must be the reason why monomerization does not take place even more readily. The difference of 0·072 Å between the two interpyrimidine bonds in the largest observed so far. A length of 1·66 (3) Å was recently reported for the C(6)–C(6′) bond in the *cis-syn* dimer of 1,3-dimethylthymine (Camerman & Camerman, 1970), but the actual value is somewhat doubtful in view of the low accuracy; one would, in fact, expect the bond to be shorter than the C(5)–C(5′) bond, reported as 1·60 (3) Å, which is more affected by overcrowding.

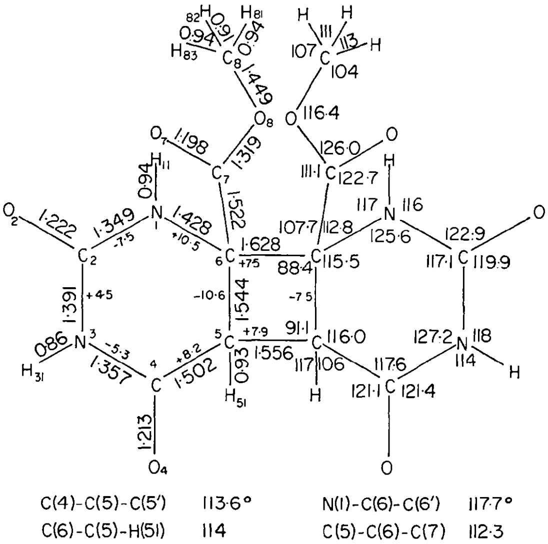

Fig. 2. Bond lengths, bond angles, and torsional angles. In bond lengths not involving H atoms, all e.s.d.'s are 0·002 Å except in C(8)–O(8) where the e.s.d. = 0·003 Å. The e.s.d.'s in corresponding bond angles are in the range 0·11–0·16°. The e.s.d.'s are 10–15 times higher when H atoms are involved.

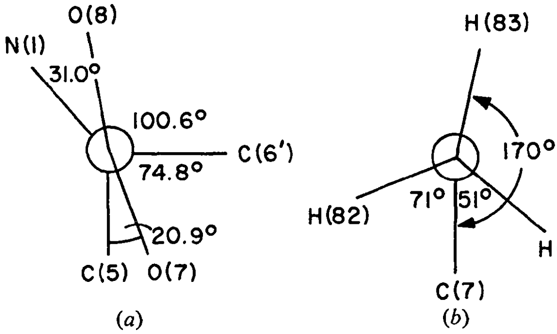

Fig. 3. Newman projections (*a*) along the C(7)–C(6) bond and (*b*) along the C(8)–O(8) bond.

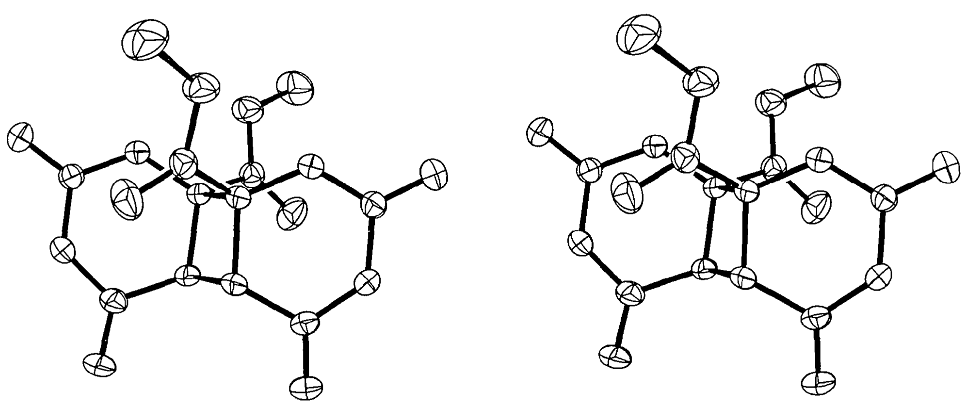

Fig. 1. Stereoscopic view of the structure; the ellipsoids enclose 50% probability.

Table 4. *Comparison of some geometrical features in pyrimidine photodimers*

Structure	N(1)–C(2)	C(2)–N(3)	N(3)–C(4)	C(4)–C(5)	C(5)–C(6)	C(6)–N(1)	Inter-pyrimidine	Twist*	Pucker†	Δ[C(6)]‡
trans-anti Methylthymine^a	1·346 (3)	1·395 (3)	1·370 (3)	1·507 (3)	1·543 (3)	1·451 (3)	1·567 (3)	None	None	
trans-anti Thymine^b	1·334 (3)	1·390 (3)	1·357 (3)	1·508 (3)	1·547 (3)	1·440 (3)	1·587 (3)	None	None	
cis-anti Dimethylthymine^c	1·342 (3) 1·344 (3)	1·426 (3) 1·406 (3)	1·378 (3) 1·377 (3)	1·509 (3) 1·503 (3)	1·533 (3) 1·529 (3)	1·431 (3) 1·449 (3)	1·571 (3) 1·577 (3)	29°	154°	0·4
cis-syn Dimethylthymine^d	1·29 (3) 1·32 (3)	1·44 (3) 1·42 (3)	1·41 (3) 1·35 (3)	1·48 (3) 1·52 (3)	1·55 (3) 1·58 (3)	1·42 (3) 1·45 (3)	1·60 (3) 1·66 (3)	26	153	0·32 0·37
cis-syn Uracil^e	1·336 (3) 1·330 (3)	1·390 (3) 1·398 (3)	1·360 (3) 1·364 (3)	1·498 (3) 1·497 (3)	1·540 (3) 1·533 (3)	1·441 (3) 1·435 (3)	1·572 (3) 1·563 (3)	24	155	0·26 0·28
cis-anti Uracil^f	1·320 (8) 1·350 (8)	1·390 (8) 1·420 (8)	1·390 (8) 1·360 (8)	1·500 (8) 1·510 (8)	1·540 (8) 1·560 (8)	1·450 (8) 1·420 (8)	1·590 (8) 1·600 (8)	21	150	0·35 0·38
cis-syn 6-Methyluracil^g	1·337 (8) 1·327 (8)	1·402 (8) 1·405 (8)	1·364 (8) 1·364 (8)	1·507 (8) 1·501 (8)	1·543 (8) 1·565 (8)	1·459 (8) 1·432 (8)	1·546 (8) 1·586 (8)	16	162	0·28
trans-syn Methyl orotate^h	1·349 (2)	1·391 (2)	1·357 (2)	1·502 (2)	1·544 (2)	1·428 (2)	1·556 (2) 1·628 (2)	7	170	0·11

a. C. H. Wei & J. R. Einstein, private communication
b. Camerman & Nyburg (1969)
c. Camerman, Weinblum & Nyburg (1969)
d. Camerman & Camerman (1970)
e. Adman & Jensen (1970)
f. Konnert & Karle (1971)
g. Gibson & Karle (1971)
h. This work

* Relative twist of two pyrimidine rings.

† Puckering of the cyclobutane ring.

‡ Deviation (in Å) of C(6) from the mean plane through the other five atoms. The second value for *cis-syn* dimethylthymine refers to C(5′).

There is an extensive network of intermolecular hydrogen bonds in the crystal structure (Fig. 4). Each dimer molecule is connected to two others in adjoining cells along *y* by pairs of strong N(1)$\cdots$O(4) bonds. The same molecules are also joined *via* water molecules, each of which is hydrogen-bonded to two pyrimidine rings separated by *b*. N(3) donates a hydrogen atom to O(*W*) which, in turn, donates H(*W*1) to O(2) and O(4) in different molecules. The presence of the asymmetric bifurcated hydrogen bond is manifested by the coplanarity of H(*W*1) with O(*W*) and the two oxygen atoms acting as acceptors. Also, the angles C(2)=O(2)$\cdots$H(*W*1) (130°) and C(4)=O(4)$\cdots$H(*W*1) (113°) do not deviate much from the ideal value of 120°. The geometry, which includes a fairly long H(*W*1)$\cdots$O(4) distance (2·42 Å), is very similar to that found in crystals of α-glycine (Albrecht & Corey, 1939; Marsh, 1958). The fact that the dihedral angle between plane *A* (which is almost parallel to *y*) and plane *E* is only 23° (Table 5) indicates the possibility that the hydrogen bond system imposes near-planarity on the pyrimidine rings, enabling each of them to participate in five intermolecular hydrogen bonds. Each water molecule also joins a pair of pyrimidine rings to a third molecule of the photodimer (related to the others by a *c* glide plane) by donating its second proton to O(7) in the ester group. This bond is quite weak, as indicated by the O(7)$\cdots$H(*W*2) and O(7)$\cdots$O(*W*) distances. In fact, it is too weak to confine the hydrogen atom to a unique position. The positive peak in the final difference Fourier map appears to be due to a position partially occupied by H(*W*2). In this minor position, the proton is hydrogen-bonded to O($W^{\rm IV}$), the oxygen atom (at $\frac{1}{2}-x,\frac{3}{2}-y,\bar{z}$) of another water molecule. Although this hydrogen bond is stronger than the one between H(*W*2) and O(7), it cannot exist throughout the crystal structure. A full occupancy of the minor position by H(*W*2) would require two symmetry-related protons to be separated by no more than 1·4 Å, clearly an impossible situation. The disorder of H(*W*2) is also indicated by the high value of its temperature parameter. On the other hand, the existence of some interaction of H(*W*2), when in its major position, with O(7) is suggested by the coplanarity of the proton with C(7), O(7), and O(*W*), and by the fact that all angles, including C=O$\cdots$H (121°), are normal for a 'linear' hydrogen bond. [Donohue's (1968) argument against the significance of the C=O$\cdots$H angle in hydrogen bonds is somewhat

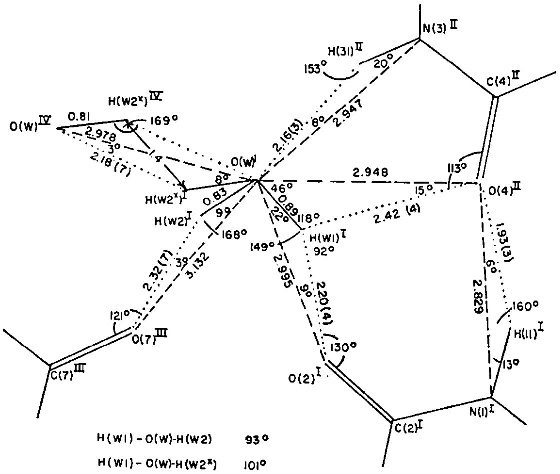

Fig. 4. Schematic diagram of the hydrogen bond system. H(*W*2$^{\times}$) refers to the minor position of the disordered atom. The e.s.d.'s in distances not in volving H atoms are 0·002–0·003 Å.

I: x, y, z III: $x, 1-y, -\frac{1}{2}+z$
II: $x, 1+y, z$ IV: $\frac{1}{2}-x, \frac{3}{2}-y, \bar{z}$

Table 5. *Least-squares planes and deviations of atoms from them*

The e.s.d.'s on *Δ* are 0·001–0·002 Å for 'heavy' atoms and 0·03–0·05 Å for H atoms.

Plane *A*		Plane *B*		Plane *C*		Plane *D*		Plane *E*		Plane *F*	
	Δ		*Δ*		*Δ*		*Δ*		*Δ*		*Δ*
N(1)	−0·036 Å	N(1)	0·000 Å	C(5)	+0·053 Å	C(6)	+0·006 Å	O(2)	0·000 Å	C(7)	0·000 Å
C(2)	+0·009	C(2)	+0·011	C(6)	−0·050	C(7)	−0·024	O(4)	0·000	O(8)	0·000
N(3)	−0·004	N(3)	−0·019	C(6′)	+0·050	O(8)	+0·009	O(*W*)	0·000	O(*W*)	0·000
C(4)	+0·024	C(4)	+0·023	C(5′)	−0·053	O(9)	+0·008	H(11)	−0·01	H(*W*2)	0·00
C(5)	−0·046	C(5)	−0·009					H(*W*1)	+0·06		
C(6)	+0·052	C(6)†	+0·110					N(1)†	+0·210		
O(2)†	+0·033	O(2)†	+0·019					C(2)†	+0·336		
O(4)†	+0·090	O(4)†	+0·071					C(4)†	−0·497		
H(11)†	+0·10										
H(31)†	+0·06										
$\chi^2=2930$		$\chi^2=415$		$\chi^2=4368$		$\chi^2=286$		$\chi^2=1·9$		$\chi^2=0$	

Dihedral angles: *A–C* 62·6°; *A–D* 36·3°; *A–E* 23·3°; *C–D* 97·6°; *E–F* 93·0°

Plane *A* $0·6214X-0·1163Y+0·7748Z=3·0159$
Plane *B* $0·6382X-0·1279Y+0·7592Z=2·9697$
Plane *C* $0·4013X-0·9159Z=-4·2042$
Plane *D* $0·9194X-0·2959Y+0·2590Z=0·1324$
Plane *E* $0·6856X+0·2693Y+0·6763Z=4·0748$
Plane *F* $0·2621X+0·8169Y-0·5138Z=4·8305$

X is along the *a* axis, *Y* is in the *ab* plane, and *Z* is along the *c** axis.

† Not included in the calculation of the plane.

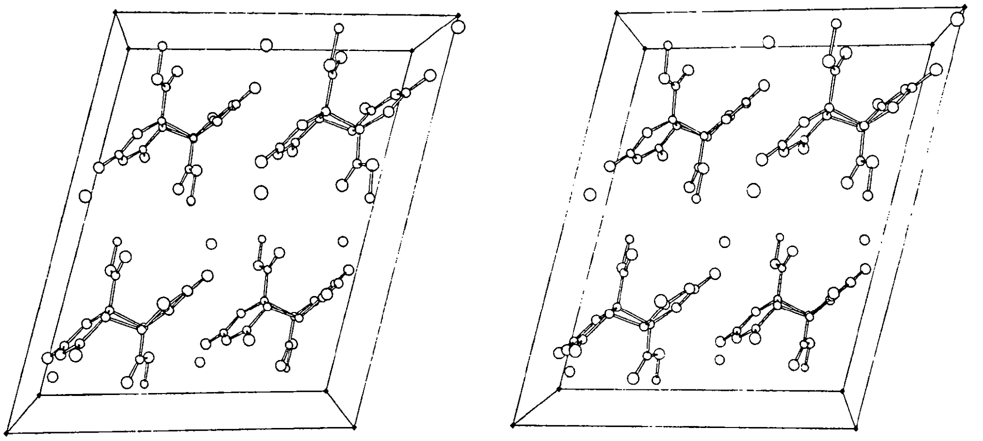

Fig. 5. Stereoscopic view along y of the contents of a unit cell. The directions of axes are $x \rightarrow$ (from −0·25 to +0·75) and $z \swarrow$ (0 to 1·0).

weakened by the fact that the angles which he quoted involved the hydrogen donor rather than the hydrogen atom itself. In view of the deviation of such bonds from linearity, the listed angles could differ from the pertinent ones by 20°. For the same reason one would expect the hydrogen atom rather than its donor to be in or near the carbonyl plane.]

Apart from the hydrogen bonds, the closest intermolecular contacts involve pyrimidine rings related by twofold screw axes. The shortest such distance is C(4)···O(2), 3·059 (2) Å. The crystal structure may be described as consisting of layers perpendicular to x, formed by hydrogen-bonded dimer and water molecules. The fairly short distance between layers along x (approximately 3 Å) may be attributed to the occasional hydrogen bonds in which H(W2) is involved. Fig. 5 shows the contents of a unit cell.

I wish to thank Drs J. M. Dunston and A. G. Szabo for supplying me with the crystals used in this structure analysis. My thanks are also due to Dr M. Przybylska for her continued encouragement and interest in this work. The *MGTLS* program of V. Schomaker and K. N. Trueblood was used in the thermal vibration analysis; Figs. 1 and 5 were drawn with the help of the *ORTEP* program of C. K. Johnson (1965). In all other computations the programs of Ahmed, Hall, Pippy & Huber (1966) were used.

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