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The Crystal and Molecular Structure of a Thymine Photodimer (Dimer '*E*')

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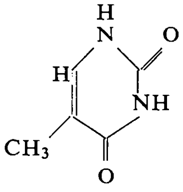
Thymine photodimer '*E*' ($C_{10}H_{12}N_4O_4$) is monoclinic with two molecules in the unit cell, space group $P2_1/c$, with dimensions $a=7{\cdot}08\pm0{\cdot}005$, $b=11{\cdot}67\pm0{\cdot}01$, $c=6{\cdot}85\pm0{\cdot}01$ Å, $\beta=105{\cdot}6\pm0{\cdot}1°$. The dimer has a centre of symmetry and consists of two 'head to tail' thymine rings, *trans* to each other, joined by a cyclobutane linkage across their 5,6 double bonds. The data were collected on an automatic four-circle diffractometer with Cu *Kα* radiation, and the phases were determined by the symbolic addition procedure. Refinement was by full-matrix anisotropic least squares to an *R* value of 0·048. The cyclobutane bond lengths are 1·547 and 1·587 Å (±0·003 Å) and the angle between the planes of the thymine and cyclobutane rings is 113·7°. A hydrogen-bonding system holds the dimers in an intermolecular network in two directions.

Introduction

Dimers of thymine(I) were first isolated and identified by Beukers, IJlstra & Berends (1960) as ultraviolet photoproducts from frozen aqueous solutions of thymine and from aqueous solutions of deoxyribonucleic acid (DNA). Wacker, Dellweg & Weinblum (1960) obtained evidence for the production of dimerized thymine in irradiated bacteria *in vivo*, and the role played by thymine dimers in the biological effects of ultraviolet irradiation has been the subject of much interest and study. Although much is known about the production and biological properties of thymine dimers, the exact structure of a dimer has never been determined. Beukers & Berends (1960) suggested the dimer was formed by linking of two thymines by a cyclobutane ring formed across their 5,6 double bonds, and Wulff & Fraenkel (1961) pointed out that *cis*-linkage of the thymines to the cyclobutane ring would give rise to four stereoisomeric dimers (I to IV, Fig. 1). Weinblum & Johns (1966) obtained four different thymine dimers (*A* to *D*) from ultraviolet irradiation of frozen thymidine solutions and thymidylyl-(3′-5′)-thymidine, and from chemical and spectroscopic evidence tentatively assigned to these the four isomeric structures of Wulff & Fraenkel (1961).

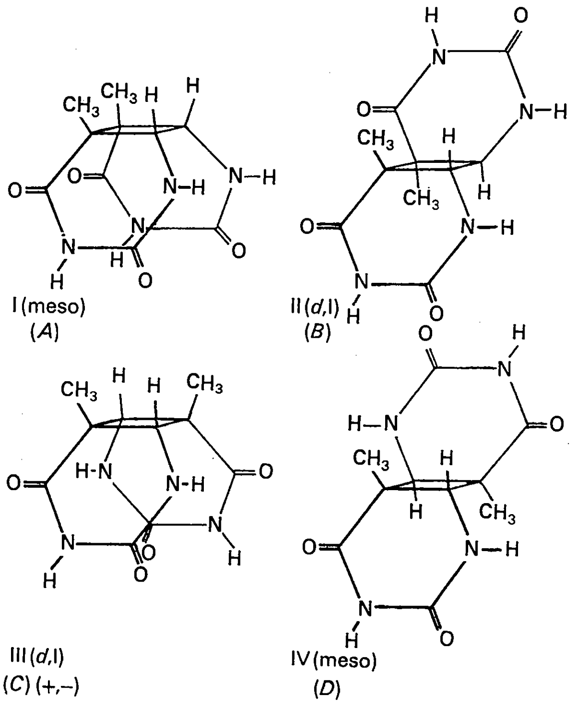


(I)

We found that one of the chromatographic fractions, *D*, of Weinblum & Johns (1966), assigned structure IV of Wulff & Fraenkel (1961), contained two crystal species, one triclinic and one monoclinic (now called '*E*'), and we undertook a full crystal-structure investigation of the monoclinic form to obtain unequivocally the molecular structure of a thymine dimer (Camerman, Nyburg & Weinblum, 1967).

Experimental

Crystals of the thymine dimer were prepared by Dr D. Weinblum by ultraviolet irradiation of frozen thymidine solutions and subsequent hydrolysis of the glycosidic bonds. Crystallization was from aqueous solution, and produced a mixture of triclinic and mono-


I (meso) (*A*)

II (*d,l*) (*B*)

III (*d,l*) (*C*) (+,−)

IV (meso) (*D*)

Fig. 1. Isomeric forms of thymine dimer according to Wulff & Fraenkel (1961).

clinic crystals in the same crystallization dish, the latter being chosen for the present detailed analysis. The unit-cell dimensions were determined from Weissenberg photographs, and, for the monoclinic crystals, refined from diffractometer measurements by a least-squares procedure (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å). The crystal data are given in Table 1.

Table 1. *Crystal data*

	Thymine dimer D*	Thymine dimer E
Formula	$C_{10}H_{12}N_4O_4$	
M.W.	252·2	
Crystal system	Triclinic	Monoclinic
a (Å)	7·5	7·08 ± 0·005
b (Å)	6·7	11·67 ± 0·01
c (Å)	8·2	6·85 ± 0·01
α	70°	—
β	131°	105·6° ± 0·1
γ	115°	—
V (Å^3)	282	545·1
Z	1	2
D_x (g.cm^{-3})	1·485	1·536
$F(000)$	132	264
μ (for Cu $K\alpha$) (cm^{-1})	10·1	10·4
Space group	$P\bar{1}$	$P2_1/c$

* We use the name dimer D to refer to the triclinic crystals obtained from the chromatographic fraction D (see text) in order to differentiate them from the monoclinic crystals (dimer E) from the same fraction.

The intensities were collected on a Picker four circle automatic diffractometer (Ni-filtered Cu radiation), and all independent reflexions with 2θ (Cu $K\alpha$) $\le 133°$ (corresponding to a minimum interplanar spacing of 0·84 Å) were measured. The moving-crystal moving-counter technique was employed (2θ scan) with stationary counts for background radiation on each side of the reflexion. The crystal used was mounted with a^* parallel to the φ axis of the goniostat, and was a roughly equidimensional prism of side 0·15 mm; absorption is low, and no corrections were considered necessary. A total of 833 reflexions were observed, which is 87·4% of the total number (953) in the range $0 < 2\theta$ (Cu $K\alpha$) $\le 133°$.

Phase determination

The structure amplitudes were put on an absolute scale by the use of a K curve (Karle & Hauptman, 1953), using a computer program which fits the best curve of the type $K = A \exp(B \sin^c\theta)$ to the experimental points, for varying values of c; in this case the best fit occurred with $c = 4$. The normalized structure amplitudes, $|E_h|$, were computed, the formula for space group $P2_1/c$ being

$$E_h^2 = \frac{F_h^2}{\varepsilon \sum_{j=1}^{N} f_{jh}^2},$$

where $\varepsilon = 2$ when h is $h0l$ or $0k0$ and $\varepsilon = 1$ otherwise; f_{jh} is the atomic scattering factor for the jth atom, N is the number of atoms in the unit cell, and the F_h^2 have been put on an absolute scale by means of the K-curve. Table 2 shows the theoretical and experimental statistical averages and distributions of the $|E|$'s.

Table 2. *Statistical averages and distributions of normalized structure amplitudes*

	Experimental	Theoretical centrosymmetric
$\langle \lvert E \rvert \rangle$	0·798	0·798
$\langle \lvert E^2 - 1 \rvert \rangle$	0·990	0·968
$\langle \lvert E \rvert^2 \rangle$	1·001	1·000
$\lvert E \rvert > 3$	0·6%	0·3%
$\lvert E \rvert > 2$	5·4%	5·0%
$\lvert E \rvert > 1$	29·7%	32·0%

The symbolic addition procedure (Karle & Karle, 1966) was used to determine the phases. The reflexions were divided into three groups: $|E'| \ge 1{\cdot}95 > |E''| \ge 1{\cdot}5 > |E'''|$, and only the 59 planes in the first group were used in the initial phase determination procedure (the value of $E \ge 1{\cdot}95$ was chosen as it gave a set with fair representation from each of the eight parity groups). Application of the Σ_2 formula,

$$sE_h \sim s \sum_k E_k E_{h-k}$$

(where s means 'sign of'), to three origin-specifying planes, and iterative re-cycling led to signs for 34 of the 59 planes, and introduction of one symbol led to signs (+, −, or $\pm a$) for all 59, 56 of them with probability $> 0{\cdot}98$. These 56 reflexions were now used in the Σ_2 formula to generate signs for the group of 61 planes with $1{\cdot}95 > |E| \ge 1{\cdot}50$; 50 of these were determined with confidence (multiple indications of the same phase) in one cycle, and no recycling was done as there were now 109 phases assigned for a 9 (non-hydrogen) atom asymmetric unit.

A strong indication that the symbol a was negative was obtained from application of the Σ_3 test:

$$sE_{2h} \sim s \sum_k E_{2k}(E_{h+k}^2 - 1),$$

accordingly only one three-dimensional E-map was computed. This revealed the structure clearly. Structure factors were calculated from coordinates of all nine non-hydrogen atoms ($R = 32{\cdot}6\%$) using scattering factors from *International Tables for X-ray Crystallography* (1962), and a second three-dimensional Fourier with all 833 terms was very clean. Inspection of the signs of the reflexions revealed that 108 of the 109 assigned phases were correct; one of the three signs for which $P < 0{\cdot}98$ in the $|E| \ge 1{\cdot}95$ group was wrong.

Refinement

The atomic coordinates and thermal parameters were refined by full-matrix least squares using a modified version of the ORFLS program (Busing, Martin &

Levy, 1962). Three cycles of refinement with isotropic thermal parameters lowered R to 18·0%, and two anisotropic cycles dropped R to 8·9% for the observed reflexions, the shifts in the last cycle being at most 2% of the standard deviation of the parameters. A three-dimensional difference Fourier was calculated, and all six hydrogen atoms were easily located as the six largest peaks on the map. The hydrogens were in-

Table 3. *Observed and calculated structure amplitudes*

Each line consists of the indices k and l, $10|F_o|$, and $10F_c$. Reflexions marked with an asterisk were unobservably weak and were assigned one half the minimum observable intensity.

	h = 0			
	0	2	167	163
	0	4	244	243
	0	6	17	11
	1	1	437	476
	1	2	116	118
	1	3	188	-175
*	1	4	11	6
	1	5	131	-144
	1	6	18	-18
	1	7	24	15
	2	0	574	644
	2	1	47	-55
	2	2	14	8
	2	3	57	55
	2	4	151	-152
	2	5	147	-149
	2	6	48	-56
	2	7	85	-90
	3	1	207	-212
	3	2	179	178
	3	3	246	-243
	3	4	21	18
	3	5	296	-298
	3	6	37	-39
	3	7	13	17
	4	0	82	-81
	4	1	116	-111
	4	2	192	184
	4	3	106	99
	4	4	181	-182
	4	5	157	-162
	4	6	16	19
	4	7	87	-91
	5	1	192	187
	5	2	256	252
	5	3	62	63
	5	4	18	-16
	5	5	29	-22
	5	6	30	26
	5	7	24	25
	6	0	164	163
	6	1	121	117
	6	2	35	35
	6	3	63	59
	6	4	37	35
	6	5	49	-50
*	6	6	11	14
	6	7	27	-28
	7	1	32	34
	7	2	179	175
	7	3	21	-25
	7	4	68	-66
	7	5	59	62
	7	6	51	48
	8	0	43	-50
	8	1	77	78
	8	2	62	-70
	8	3	31	-31
	8	4	37	37
	8	5	40	-41
	8	6	43	-35
	9	1	28	24
*	9	2	12	-18
	9	3	38	39
	9	4	65	-67
	9	5	63	65
	10	0	40	-46
	10	1	58	-57
	10	2	81	75
	10	3	25	-28
	10	4	41	35
	10	5	83	-81
	11	1	14	-13
	11	2	48	-51
	11	3	20	21
	11	4	28	-30
	12	0	98	-92
	12	1	31	-22
	12	2	20	-18
	12	3	16	-13
	13	1	57	-58
	13	2	16	-14
	h = 1			
*	0	-8	8	-9
	0	-6	82	-85
	0	-4	444	-448
	0	-2	553	-569
	0	0	14	-20
*	0	2	3	-2
	0	4	78	-73
	0	6	49	-43
*	1	-8	5	3
	1	-7	127	116
	1	-6	40	-43
*	1	-5	12	9
	1	-4	36	-29
	1	-3	427	-425
	1	-2	169	-166
	1	-1	318	324
	1	0	284	-298
	1	1	327	-323
	1	2	28	-23
	1	3	49	47
	1	4	103	-103
	1	5	202	-202
	1	6	40	37
	1	7	113	-111
*	2	-7	6	-7
	2	-6	48	-48
*	2	-5	6	13
	2	-4	89	-85
	2	-3	150	146
	2	-2	44	-47
	2	-1	304	-316
	2	0	412	425
	2	1	245	241
	2	2	454	453
	2	3	95	-94
	2	4	99	98
	2	5	65	63
	2	6	108	110
*	2	7	5	-3
	3	-7	94	94
	3	-6	24	-26
	3	-5	29	-25
	3	-4	84	-83
	3	-3	134	135
	3	-2	87	-87
	3	-1	213	216
	3	0	512	-543
	3	1	576	582
	3	2	19	19
	3	3	129	131
	3	4	122	-119
	3	5	94	96
	3	6	51	51
	3	7	26	-25
*	4	-7	12	-19
	4	-6	111	-115
	4	-5	147	145
	4	-4	44	-43
	4	-3	63	63
	4	-2	77	-78
	4	-1	191	183
	4	0	242	246
	4	1	47	39
	4	2	150	153
	4	3	79	75
	4	4	22	13
	4	5	67	68
	4	6	84	87
*	4	7	5	-10
	5	-7	45	-48
	5	-6	70	72
	5	-5	131	-133
*	5	-4	8	-1
	5	-3	132	-134
	5	-2	32	33
	5	-1	32	-34
	5	0	213	-210
	5	1	58	59
	5	2	16	16
	5	3	120	-121
	5	4	40	-36
	5	5	49	52
	5	6	34	-32
	6	-7	26	-28
	6	-6	37	-35
	6	-5	242	245
	6	-4	82	-80
*	6	-3	6	-1
	6	-2	33	-36
	6	-1	226	225
	6	0	46	43
	6	1	71	65
	6	2	160	-164
	6	3	31	26
	6	4	14	-15
	6	5	24	17
	6	6	50	-44
	7	-6	44	48
	7	-5	13	-3
	7	-4	90	93
*	7	-3	6	6
	7	-2	18	-17
	7	-1	166	164
	7	0	39	44
	7	1	27	-22
	7	2	26	-26
	7	3	37	37
	7	4	50	-51
*	7	5	8	2
	7	6	59	-53
	8	-6	41	46
	8	-5	77	76
	8	-4	16	-7
*	8	-3	13	8
	8	-2	161	166
*	8	-1	3	12
	8	0	35	35
	8	1	96	97
	8	2	16	-17
	8	3	48	-54
	8	4	15	7
*	8	5	6	-7
	8	6	34	-35
	9	-6	32	-32
	9	-5	38	-39
	9	-4	16	-13
	9	-3	42	38
	9	-2	32	-32
*	9	-1	12	7
*	9	0	12	11
	9	1	15	-14
	9	2	19	19
	9	3	19	-13
	9	4	68	-68
	9	5	40	-35
	10	-5	62	-67
	10	-4	57	-54
*	10	-3	11	-14
	10	-2	24	21
	10	-1	32	-29
	10	0	65	-72
	10	1	41	40
	10	2	34	-33
	10	3	22	-31
	10	4	44	-47
	10	5	52	-51
	11	-4	48	-49
	11	-3	13	5
	11	-2	22	20
	11	-1	39	-42
*	11	0	4	12
	11	1	32	30
	11	2	25	25
	11	3	38	-36
	11	4	81	-80
	12	-4	25	32
*	12	-3	7	4
	12	-2	19	16
	12	-1	47	44
	12	0	52	42
	12	1	38	32
	12	2	18	20
	12	3	28	-31
	13	-2	24	29
	13	-1	24	16
	13	0	74	79
	13	1	50	49
*	13	2	5	0
	h = 2			
	0	-8	43	41
	0	-6	58	-77
	0	-4	136	-129
	0	-2	113	113
	0	0	341	-333
	0	2	198	196
	0	4	119	118
	0	6	175	164
	1	-8	12	11
*	1	-7	6	-2
	1	-6	23	-22
	1	-5	66	67
	1	-4	128	125
	1	-3	137	134
	1	-2	85	-86
	1	-1	266	262
	1	0	461	470
	1	1	166	169
	1	2	139	-140
	1	3	151	149
	1	4	60	54
	1	5	238	249
*	1	6	9	-9
*	1	7	7	-1
	2	-8	23	17
	2	-7	113	-95
	2	-6	109	-118
	2	-5	24	20
	2	-4	209	-204
	2	-3	33	35
	2	-2	229	-223
	2	-1	249	248
	2	0	546	-561
	2	1	360	369
	2	2	168	-161
	2	3	67	-64
	2	4	45	-43
	2	5	142	142
	2	6	33	27
	2	7	22	29
*	3	-7	6	-6
	3	-6	17	7
*	3	-5	6	-6
	3	-4	81	78
	3	-3	124	-117
	3	-2	135	137
	3	-1	33	-40
	3	0	330	328
	3	1	139	-134
	3	2	226	-223
	3	3	68	-68
	3	4	31	-33
	3	5	63	70
	3	6	54	-55
	4	-7	60	-66
	4	-6	30	27
	4	-5	96	-97
	4	-4	59	-58
	4	-3	69	70
	4	-2	57	51
	4	-1	134	130
	4	0	13	2
	4	1	146	145
	4	2	101	-93
	4	3	117	-113
	4	4	41	43
	4	5	14	4
	4	6	40	-39
	5	-7	53	47
	5	-6	62	60
	5	-5	43	45
	5	-4	154	-153
*	5	-3	4	-8
	5	-2	277	270
	5	-1	304	296
	5	0	110	-115
	5	1	79	78
	5	2	82	-77
	5	3	135	132
	5	4	158	-165
	5	5	62	60
	5	6	54	-52
	6	-7	47	-40
	6	-6	27	25
	6	-5	125	-124
	6	-4	66	-63
	6	-3	29	-31
	6	-2	80	78
	6	-1	36	29
	6	0	181	180
	6	1	32	27
	6	2	47	50
	6	3	89	-89
	6	4	78	74
	6	5	61	-56
*	6	6	9	-12
*	7	-7	11	-15
	7	-6	14	13
	7	-5	140	-141
	7	-4	120	-123
	7	-3	129	-136
	7	-2	72	69
	7	-1	60	-64
	7	0	41	40
	7	1	15	-11
*	7	2	6	-36
	7	3	24	21
	7	4	89	-96
	7	5	28	-30
	8	-6	85	-85
	8	-5	24	-26
	8	-4	104	-100
	8	-3	32	-36
	8	-2	128	-127
	8	-1	43	49
*	8	0	9	12
	8	1	89	93
*	8	2	7	27
	8	3	71	-74
	8	4	42	-44
	8	5	23	-17
*	9	-6	5	-4
	9	-5	108	-111
	9	-4	29	22
	9	-3	15	-13
	9	-2	20	7
	9	-1	82	-90
	9	0	170	171
	9	1	110	105
*	9	2	6	2
	9	3	14	-10
*	9	4	11	-9
	9	5	21	-15
	10	-5	22	19
	10	-4	13	24
	10	-3	22	13
*	10	-2	6	3
	10	-1	70	73
	10	0	111	112
	10	1	112	113
	10	2	67	67
*	10	3	6	-4
	10	4	15	15
	11	-4	12	3
	11	-3	18	19
	11	-2	15	7
	11	-1	30	23
	11	0	89	93
	11	1	54	55
	11	2	54	55
	11	3	24	20
	12	-3	31	-34
	12	-2	24	-23
	12	-1	21	19
	12	0	26	22
	12	1	44	41
	12	2	25	-24
	13	-2	29	-29
	13	-1	17	-8
*	13	0	9	6
	13	1	42	-42
	h = 3			
	0	-8	40	36
	0	-6	31	19
	0	-4	86	-94
	0	-2	112	115
	0	0	187	-178
	0	2	388	-390
*	0	4	12	10
	0	6	88	-86
*	1	-8	10	7
	1	-7	106	-94
	1	-6	74	76
	1	-5	74	-74
	1	-4	68	-62
	1	-3	13	-2
*	1	-2	8	5
	1	-1	117	119
	1	0	129	127
	1	1	72	-69
	1	2	103	-101
	1	3	27	-26
	1	4	27	-25
	1	5	134	136
	1	6	76	-81
	2	-8	71	71
	2	-7	21	18
	2	-6	39	33
	2	-5	53	-57
	2	-4	36	43
	2	-3	288	-282
	2	-2	262	257
	2	-1	110	109
	2	0	41	32
	2	1	180	-181
	2	2	86	-82
	2	3	21	-18
	2	4	95	96
	2	5	145	-146
	2	6	25	24
	3	-7	13	-16
	3	-6	60	66
	3	-5	103	-108
	3	-4	93	-94
	3	-3	132	129
	3	-2	60	58
	3	-1	65	-67
	3	0	311	308
	3	1	124	124
	3	2	27	-23
	3	3	41	38
	3	4	27	-27
	3	5	144	142
	3	6	70	-72
	4	-7	32	32
	4	-6	53	-54
	4	-5	224	-229
	4	-4	122	-121
	4	-3	112	-110
*	4	-2	5	-3
	4	-1	34	-32
	4	0	170	-172
	4	1	116	115
	4	2	26	-22
	4	3	17	-15
*	4	4	9	15
	4	5	83	-67
	4	6	45	44
	5	-7	17	15
	5	-6	38	-36
	5	-5	168	-172
	5	-4	60	-68
	5	-3	136	-133
	5	-2	18	27
	5	-1	252	-255
	5	0	320	320
	5	1	183	-181
	5	2	122	120
	5	3	43	-45
	5	4	21	-17
*	5	5	8	-7
	6	-7	40	36
	6	-6	20	5
	6	-5	183	-183
	6	-4	92	-89
	6	-3	24	-27
	6	-2	65	-65
	6	-1	34	-27
	6	0	99	-101
	6	1	216	214
	6	2	25	26
	6	3	61	-62
	6	4	29	31
*	6	5	12	-7
	7	-6	18	-18
	7	-5	85	88
	7	-4	40	-41
	7	-3	35	-31
	7	-2	16	-10
	7	-1	61	55
	7	0	250	250
*	7	1	6	-2
	7	2	31	24
	7	3	101	100
*	7	4	10	19
	7	5	23	17
	8	-6	74	70
	8	-5	51	-45
	8	-4	100	100
	8	-3	60	-65
	8	-2	19	-21
	8	-1	75	76
	8	0	128	130
	8	1	43	44
	8	2	104	108
	8	3	33	-24
	8	4	92	96
*	9	-6	5	-1
	9	-5	74	72
	9	-4	68	-68
	9	-3	46	-49
	9	-2	14	-17
*	9	-1	13	-15
	9	0	77	77
	9	1	31	29
	9	2	24	-28
	9	3	53	46
*	9	4	9	7
	10	-5	39	-34
*	10	-4	5	-5
	10	-3	60	-62
	10	-2	136	-140
	10	-1	39	34
	10	0	29	-23
	10	1	40	-38
*	10	2	3	-1
*	10	3	7	5
	11	-4	46	-54
	11	-3	64	-67
	11	-2	20	7
	11	-1	79	-71
	11	0	13	-9
	11	1	30	-33
	11	2	22	12
	11	3	22	21
*	12	-3	9	-5
	12	-2	32	-32
	12	-1	19	19
	12	0	41	-34
	12	1	26	20
	h = 4			
	0	-6	132	146
	0	-4	29	-29
	0	-2	254	257
	0	0	18	11
	0	2	95	101
	0	4	78	82
	1	-7	48	49
	1	-6	31	-31
	1	-5	174	-174
	1	-4	62	-61
	1	-3	53	-56
	1	-2	42	-38
	1	-1	194	-187
	1	0	24	23
	1	1	157	-154
	1	2	107	107
	1	3	59	61
	1	4	38	38
	1	5	48	-52
	2	-7	51	53
*	2	-6	11	4
	2	-5	74	-76
	2	-3	75	-77
	2	-2	98	-95
	2	-1	92	-90
	2	0	19	-10
	2	1	25	-23
	2	2	79	-79
	2	3	70	68
	2	4	45	47
*	2	-4	3	-5
*	2	5	12	9
	3	-7	22	-23
	3	-6	54	-55
	3	-5	63	-63
	3	-4	42	-39
	3	-3	66	-67
	3	-2	108	-103
	3	-1	224	-217
*	3	0	5	11
	3	1	82	-84
	3	2	142	141
	3	3	60	-57
	3	4	28	29
	3	5	20	19
	4	-7	109	109
	4	-6	21	-21
	4	-5	17	-9
	4	-4	159	163
	4	-3	63	-55
	4	-2	60	-53
	4	-1	73	-71
	4	0	161	158
	4	1	44	-42
*	4	2	6	-10
*	4	3	11	7
	4	4	126	131
	4	5	23	-23
	5	-7	51	44
*	5	-6	10	-17
	5	-5	88	89
	5	-4	25	23
	5	-3	134	136
	5	-2	94	-94
	5	-1	58	55
	5	0	66	71
	5	1	52	55
	5	2	43	39
	5	3	61	65
	5	4	28	19
	5	5	83	87
	6	-7	83	84
	6	-6	27	23
	6	-5	35	36
	6	-4	31	31
	6	-3	71	-74
	6	-2	54	49
	6	-1	65	64
	6	0	77	-82
	6	1	40	-44
	6	2	40	36
	6	3	33	30
	6	4	63	68
*	7	-6	3	3
	7	-5	16	5
	7	-4	55	-56
	7	-3	35	-35
	7	-2	58	-58
	7	-1	83	-84
	7	0	61	59
	7	1	165	-161
	7	2	21	-16
*	7	3	6	-13
	7	4	52	58
	8	-6	15	-2
	8	-5	27	-25
	8	-4	86	-84
	8	-3	80	-85
	8	-2	57	-61
	8	-1	77	71
	8	0	231	-231
	8	1	45	-48
	8	2	57	-56
	8	3	51	50
	8	4	43	-44
	9	-5	47	48
	9	-4	72	-68
	9	-3	32	-27
*	9	-2	9	-9
	9	-1	35	-32
*	9	0	11	-5
	9	1	77	-75
	9	2	22	20
	9	3	16	-13
	10	-4	54	53
*	10	-3	7	-1
	10	-2	20	12
*	10	-1	12	14
*	10	0	6	6
	10	1	40	33
	10	2	17	17
	11	-4	35	-39
	11	-3	34	34
*	11	-2	12	13
	11	-1	34	38
*	11	0	9	6
	11	1	38	39
*	12	-2	8	1
*	12	-1	4	2
*	12	0	12	12
	h = 5			
	0	-6	75	-78
	0	-4	105	102
	0	-2	168	-166
	0	0	169	-174
	0	2	88	87
	0	4	34	33
	1	-7	80	80
	1	-6	19	11
	1	-5	34	37
	1	-4	38	38
	1	-3	74	76
*	1	-2	13	15
	1	-1	215	-216
*	1	0	12	-8
	1	1	104	-102
	1	2	31	-28
	1	3	43	50
*	1	4	9	17
*	2	-7	9	-1
	2	-6	35	32
	2	-5	156	158
	2	-4	162	164
	2	-3	53	51
	2	-2	46	-40
	2	-1	142	139
	2	0	32	-19
	2	1	53	-52
	2	2	64	66
*	2	3	9	-1
	2	4	91	93
	3	-7	46	49
	3	-6	36	-35
	3	-5	178	180
	3	-4	52	53
	3	-3	27	25
	3	-2	18	15
	3	-1	42	42
	3	0	62	-59
	3	1	121	-122
	3	2	20	-24
	3	3	74	79
	3	4	45	45
	4	-7	28	-25
	4	-6	35	31
	4	-5	73	71
	4	-4	30	26
	4	-3	56	57
	4	-2	73	-72
	4	-1	41	41
	4	0	109	-113
	4	1	44	-43
	4	2	97	-98
*	4	3	10	5
	4	4	19	16
	5	-6	95	-93
	5	-5	28	26
	5	-4	42	-45
	5	-3	39	-39
	5	-2	25	-25
	5	-1	51	-51
	5	0	167	-169
	5	1	165	-168
	5	2	28	-30
	5	3	29	-26
	5	4	17	13
	6	-6	24	-18
	6	-5	34	-35
	6	-4	23	-17
*	6	-3	11	5
*	6	-2	12	5
*	6	-1	14	-17
	6	0	126	-125
	6	1	85	-88
	6	2	41	-43
*	6	3	5	-0
	6	4	39	-40
	7	-6	23	-23
	7	-5	14	-2
	7	-4	64	-65
	7	-3	119	122
	7	-2	34	34
*	7	-1	4	20
	7	0	127	-132
	7	1	80	78
	7	2	28	-27
	7	3	13	-4
	8	-5	13	-3
	8	-4	40	41
	8	-3	13	3
	8	-2	86	90
	8	-1	47	45
	8	0	45	39
	8	1	39	-36
	8	2	29	27
	8	3	24	19
*	9	-5	5	-8
*	9	-4	12	-10
	9	-3	34	37
	9	-2	26	31
	9	-1	27	19
*	9	0	6	-4
	9	1	53	51
	9	2	12	-5
	10	-4	33	-31
	10	-3	16	-11
	10	-2	18	-9
	10	-1	24	17
*	10	0	12	-7
	10	1	25	22
	11	-2	22	-24
*	11	-1	5	-1
	h = 6			
	0	-6	13	10
	0	-4	198	201
	0	-2	62	60
	0	0	75	-76
	0	2	16	-8
	1	-7	16	-25
*	1	-6	12	14
	1	-5	207	211
	1	-4	101	-97
	1	-3	130	132
	1	-2	56	55
	1	-1	54	54
	1	0	95	-93
	1	1	60	-59
	1	2	20	-19
*	1	3	6	-8
	2	-6	34	-36
	2	-5	60	-53
	2	-4	50	47
	2	-3	16	-12
	2	-2	43	-39
	2	-1	17	22
	2	0	168	-174
	2	1	69	-69
	2	2	58	-54
*	2	3	9	-5
*	3	-6	11	-5
	3	-5	51	49
	3	-4	98	-96
*	3	-3	11	10
	3	-2	64	65
	3	-1	43	-41
	3	0	122	-120
	3	1	89	-92
	3	2	71	-68
*	3	3	4	-2
	4	-6	13	-8
*	4	-5	7	-8
	4	-4	16	22
	4	-3	48	50
	4	-2	21	28
	4	-1	27	25
	4	0	97	-95
	4	1	14	11
	4	2	24	25
	4	3	44	-47
	5	-6	33	-33
	5	-5	25	20
	5	-4	44	46
	5	-3	87	92
	5	-2	54	60
*	5	-1	13	8
	5	0	23	21
	5	1	61	55
	5	2	51	-52
	5	3	32	33
*	6	-5	11	-9
	6	-4	57	56
	6	-3	73	78
	6	-2	31	29
	6	-1	30	30
	6	0	17	7
	6	1	56	61
	6	2	13	12
*	7	-5	5	-16
*	7	-4	10	11
*	7	-3	7	3
	7	-2	56	55
	7	-1	43	-50
*	7	0	9	-3
	7	1	14	10
	7	2	25	-22
*	8	-4	11	-7
	8	-3	13	5
	8	-2	43	-39
	8	-1	33	-29
	8	0	29	28
	8	1	41	-38
	9	-3	29	-27
	9	-2	19	8
	9	-1	21	22
	9	0	71	-70
	h = 7			
	0	-6	48	-44
	0	-4	76	-65
*	0	-2	8	-0
	0	0	95	-95
	0	2	45	-48
*	1	-6	5	-0
	1	-5	22	-28
	1	-4	18	4
	1	-3	22	22
	1	-2	27	22
	1	-1	16	-14
*	1	0	10	-4
	1	1	35	32
	1	2	35	35
	2	-6	26	34
	2	-5	82	-83
	2	-4	31	31
	2	-3	67	65
	2	-2	88	93
	2	-1	63	-61
	2	0	29	17
	2	1	72	74
	2	2	14	12
	3	-5	79	76
	3	-4	16	16
	3	-3	68	69
*	3	-2	13	17
	3	-1	78	75
	3	0	29	33
	3	1	74	73
	3	2	24	28
	4	-5	35	-35
	4	-4	73	72
	4	-3	16	-11
	4	-2	43	47
	4	-1	47	-48
	4	0	49	47
	4	1	13	18
	5	-5	20	20
*	5	-4	9	4
	5	-3	13	-4
	5	-2	35	-38
	5	-1	35	-38
	5	0	17	18
*	5	1	5	0
	6	-4	45	42
	6	-3	37	-39
	6	-2	35	-33
	6	-1	46	-44
*	6	0	9	8
*	7	-3	7	5
*	7	-2	5	2
	7	-1	30	-26
	h = 8			
	0	-4	72	71
*	0	-2	9	9
	0	0	167	165
	1	-4	49	52
	1	-3	14	12
	1	-2	17	-16
*	1	-1	6	-1
	1	0	18	14
	2	-4	37	-35
	2	-3	14	14
	2	-2	25	-28
	2	-1	39	-34
	2	0	50	47
	3	-3	61	-64
	3	-2	42	-43
	3	-1	36	-39
*	4	-3	5	-5
*	4	-2	4	5

cluded in structure factor calculations using the H scattering factor from *International Tables for X-ray Crystallography* (1962), with the anisotropic temperature factors of the atoms to which they were bonded ($R = 6{\cdot}9\,\%$), and two cycles of least squares (refining only the non-hydrogen parameters) lowered R to 5·0%. Additional refinement was then carried out varying all 'heavy-atom' parameters and the hydrogen positional parameters (the hydrogen thermal parameters were kept fixed with H(1) and H(3) given the anisotropic temperature factors of N(1) and N(3), and H(6) and the methyl hydrogens given isotropic temperature factors corresponding to the average of the anisotropic components of the atoms to which they were bonded). Convergence occurred ($R = 4{\cdot}8\,\%$) after three cycles of refinement, the shifts in the fourth cycle being less than 5% of the standard deviations for the 'heavy atoms', and less than 15% of the standard deviations for the hydrogens. The final observed and calculated structure factors are given in Table 3, and the positional and thermal parameters with standard deviations in Table 4. β_{ij} in Table 4 are the coefficients in the expression:

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{23}kl+2\beta_{13}hl+2\beta_{12}hk)\right].$$

The bond distances and valency angles in the molecule are shown in Fig. 2, and the intermolecular packing is shown in Fig. 3, the dashed lines representing hydrogen bonds.

The best plane through the pyrimidine nucleus and the O(2) and O(4) atoms (all atoms given equal weight) has the equation

$$-0{\cdot}6686X+0{\cdot}7120Y-0{\cdot}2146Z+0{\cdot}7395=0\,,$$

where X, Y, and Z are coordinates in Å referred to orthogonal axes a^*, b, and c' ($=c\sin\beta$). The deviations of the atoms from the plane are given in Table 5. The plane of the cyclobutane ring has equation

$$-0{\cdot}3323X-0{\cdot}9257Y-0{\cdot}1981Z=0\,.$$

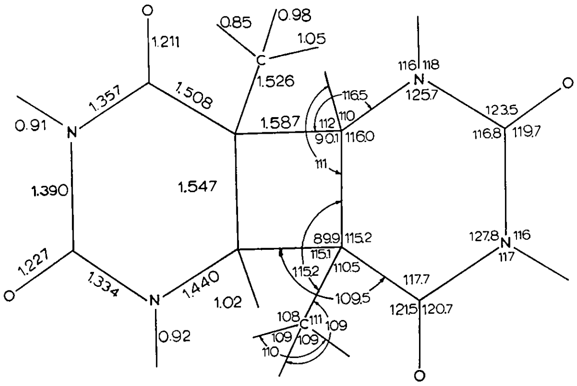


Fig. 2. Bond distances (Å) and valency angles (°) in dimer '*E*'. Standard deviations of bond lengths are 0·003 Å for bonds involving 'heavy atoms' and 0·03 Å for bonds involving hydrogens. Standard deviations of bond angles are 0·2° for 'heavy atom' angles, 1·4–1·6° for angles involving H(1), H(3) and H(6) and 1·8–2·8° for the methyl hydrogens.

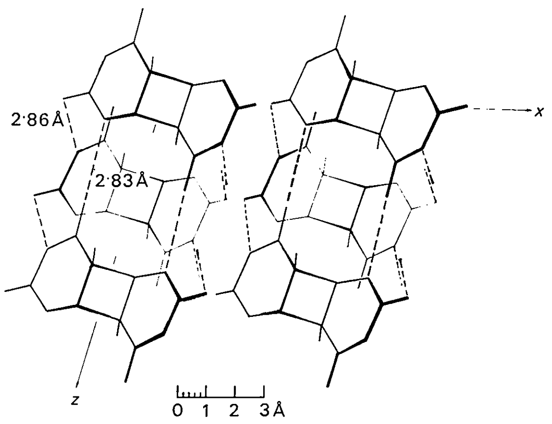


Fig. 3. Intermolecular packing viewed along [010]. The molecules halfway along z are related to those at the corners by the c-glide plane. Hydrogen bonds are shown by dashed lines, and when between a molecule and the one *above* or *below* the next one indicated in the diagram, by unterminated dashed lines. [The C(2)–O(2) bonds in the middle of the diagram have been slightly shortened for the sake of clarity].

Table 4. *Final position parameters (fractional) with standard deviations, and anisotropic thermal parameters* (× 10^5)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	0·2667 (2)	0·0549 (2)	−0·1089 (2)	1233 (40)	686 (17)	759 (36)	−158 (21)	325 (30)	−22 (20)
C(2)	0·3755 (3)	0·1260 (2)	0·0286 (3)	1122 (45)	492 (18)	1194 (47)	89 (24)	188 (36)	101 (23)
O(2)	0·4962 (2)	0·1924 (1)	−0·0075 (2)	1527 (34)	661 (14)	1772 (38)	−219 (19)	228 (27)	259 (19)
N(3)	0·3497 (3)	0·1213 (2)	0·2226 (2)	1594 (46)	745 (18)	975 (41)	−275 (23)	297 (34)	−236 (22)
C(4)	0·2332 (3)	0·0489 (2)	0·2930 (3)	1342 (50)	1103 (27)	886 (50)	−211 (30)	163 (37)	−33 (28)
O(4)	0·2305 (3)	0·0515 (2)	0·4691 (2)	2780 (53)	2556 (36)	720 (36)	−1326 (35)	571 (33)	−390 (27)
C(5)	0·1021 (3)	−0·0310 (2)	0·1429 (3)	1248 (46)	607 (19)	941 (43)	13 (23)	218 (34)	169 (22)
C(6)	0·1142 (3)	−0·0190 (2)	−0·0784 (2)	1261 (46)	484 (18)	1081 (45)	−27 (23)	292 (36)	−11 (22)
C(7)	0·1201 (4)	−0·1532 (3)	0·2254 (5)	2072 (66)	832 (26)	2827 (80)	415 (34)	1021 (61)	792 (36)
H(1)	0·273 (3)	0·062 (2)	−0·241 (4)	1080	616	879	−158	259	−91
H(3)	0·414 (4)	0·176 (2)	0·310 (4)	1483	712	919	−180	357	−130
H(6)	0·123 (4)	−0·098 (2)	−0·141 (4)	1188	406	1272	0	331	0
H(*m*1)	0·020 (5)	−0·205 (3)	0·121 (5)	2620	895	2804	0	730	0
H(*m*2)	0·086 (5)	−0·153 (3)	0·355 (5)	2620	895	2804	0	730	0
H(*m*3)	0·235 (4)	−0·179 (3)	0·243 (5)	2620	895	2804	0	730	0

Table 5. *Deviations from the pyrimidine plane*

	Deviation
N(1)	−0·048 Å
C(2)	0·003
O(2)	−0·011
N(3)	0·051
C(4)	−0·013
O(4)	−0·010
C(5)	−0·028
C(6)	0·056
H(1)	0·010
H(3)	0·188

Discussion

Because there are two dimers in the unit cell in space group $P2_1/c$ this dimer is necessarily centrosymmetric, in accordance with the assignment of Weinblum & Johns (1966). Fig. 4 shows superimposed sections of the electron-density distribution taken through the atomic centres, and confirms the thymine–thymine cyclobutane linkage which has been generally accepted, and which in this centrosymmetric dimer is a 5,6:5,6 linkage with the thymines *trans* to each other. Each thymine ring is *cis*-bonded to the cyclobutane ring.

The cyclobutane ring bond lengths are 1·547 ± 0·003 Å for the *intra* pyrimidine ring bond and 1·587 ± 0·003 Å for the *inter* thymine bond. The difference is very significant, and the lengths are similar to the *intra*- and *inter*-ring distances of 1·54 and 1·59 Å (± 0·015 Å) observed in the centrosymmetric photodimer of cyclopentenone (Margulis, 1965*a*). Poly-substituted cyclobutanes have generally exhibited longer-than-normal cyclobutane ring bonds: some distances in other centrosymmetric derivatives are 1·566 and 1·573 Å (± 0·015 Å) in tetraphenylcyclobutane (Margulis, 1965*b*), 1·552 and 1·573 Å (± 0·006 Å) in *trans*-1,3-cyclobutanedicarboxylic acid (Margulis, 1967), and 1·547 and 1·561 Å (± 0·002 Å) in tetracyanocyclobutane (Greenberg & Post, 1966). The bond distance in cyclobutane itself, determined by electron diffraction, is 1·548 ± 0·003 Å (Almenningen, Bastiansen & Skancke, 1961). Thus, it seems that a general effect of chemical substitution in cyclobutane is to cause bond lengthening, while the presence of fused-rings substituents, as in this case and the photodimer of cyclopentenone, puts a constraint on the lengthening of the *intra*-ring bond.

It is interesting to note that in all cases where the cyclobutane ring has been found to be planar it has been in a centrosymmetric molecule, and the molecule has occupied a symmetry position in the crystal structure which necessitated a flat cyclobutane. Conversely, no cyclobutane derivative has yet been structurally determined which occupies a general position in the crystal unit cell and has a planar cyclobutane ring, there always being some degree of puckering.

The N(1)–C(6) distance is 1·440 ± 0·003 Å in the dimer [*vs.* 1·382 ± 0·007 Å in thymine monohydrate (Gerdil, 1961) and 1·37 ± 0·02 Å in 5-iodo-2′-deoxyuridine (Camerman & Trotter, 1965) and calcium thymidylate (Trueblood, Horn & Luzatti, 1961)], reflecting the change in hybridization of C(6). The other bond length differences between the dimer and the above mentioned thymine derivatives are small: N(1)–C(2) is 1·334 ± 0·003 Å *vs.* 1·36–1·37 Å in the above, and C(2)–N(3) is 1·390 ± 0·003 Å, as opposed to 1·36–1·38 Å. These differences are possibly due to the strain introduced into the molecule by the formation of the cyclobutane bridge. The N–H bonds average 0·915 Å (± 0·03 Å) and the four C–H bonds average 0·98 Å.

The bond angles in the thymine moiety of the dimer differ very little from those in the above mentioned molecules except for the N(1)–C(6)–C(5) and C(6)–C(5)–C(4) angles, which are decreased to 116·0 and 115·2° (± 0·2°) (from about 122° and 118°) because of the strain of the adjacent cyclobutane angles (90°).

The thymine residue (omitting the methyl group) is approximately planar, the maximum deviations from the least-squares plane through the eight atoms being 0·06 Å for C(6) and 0·05 Å for N(3) and N(1). The two N–H hydrogens also lie approximately on this plane (Table 5). The angle between the planes of the thymine and cyclobutane rings is 113·7°.

Fig. 3 shows the packing of the dimers in the crystal. The dimer molecules are held together by hydrogen bonds between the O(4) and N(1) atoms in molecules one *c* unit cell translation apart, and by a stepwise network of hydrogen bonds in the *y* direction between O(2) and N(3) atoms in molecules related by the *c*-glide plane. Each dimer forms four such N(3)···O(2) contacts, two to the two glide-related molecules *above* it in the *y* direction (from the N(3) and O(2) at one end

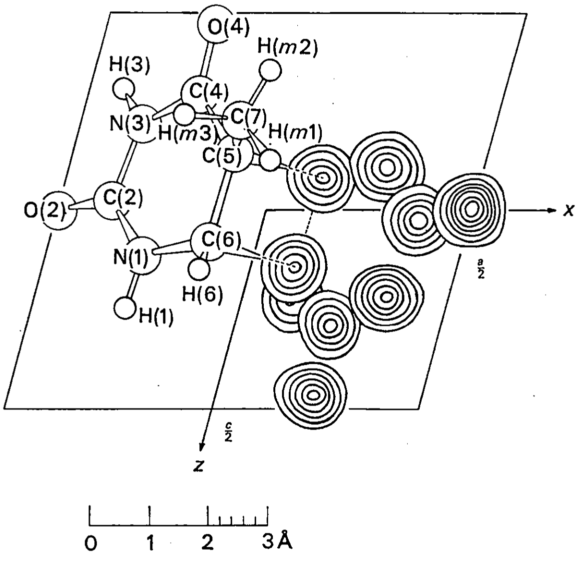


Fig. 4. Superimposed sections of the electron-density distribution, taken through the atomic centres parallel to (010). Contours are at arbitrary intervals. A perspective drawing of half of the dimer is also shown. Hydrogen positions are shown on the perspective drawing.

of the dimer), and two to the two molecules *below* it (from the N(3) and O(2) at the other end of the dimer; see Fig. 3). The O···H–N distances are 2·83 and 2·86 Å. The N(1)–H(1)···O(4) and N(3)–H(3)···O(2) bonds are slightly bent, the angles being 165° and 168° respectively (Table 6). The C(2)–O(2)···H(3) angle is 121°, close to the optimum value of 120° expected for interaction of an oxygen lone-pair of electrons with the H(3). The C(4)–O(4)···H(1) angle is not far from linear (170·5°) indicating that it is roughly the bisector of the oxygen lone-pairs which is directed toward the H-donor N(1). There are no hydrogen bonds joining molecules in the *x* direction (see Fig. 3); the crystals exhibit cleavage parallel to (100). All other approaches correspond to normal van der Waals interactions (Table 6).

Shortly after the completion of this work, Dr R. Einstein at Oak Ridge National Laboratories succeeded in solving the structure of the centrosymmetric dimer of 1-methylthymine (Einstein, 1967). The not-completely-refined bond lengths and angles differ very little from those reported here.

The triclinic crystals of this dimer are centrosymmetric, space group $P\bar{1}$ [by the $N(z)$ test] and their unit cell volume is approximately one half that of the monoclinic form; this suggests that the two crystals are polymorphic variants of the same isomer. These crystals and those of other thymine dimers are currently under study.

Note added in proof: –Since completion of this work there have appeared three papers on related photodimers: Photodimer *D* of 1-methylthymine (Einstein. Hosszu, Longworth, Rahn & Wei, 1967), photodimer *A* of 1,3-dimethylthymine (Camerman & Camerman, 1968), and photodimer *A* of uracil (Adman, Gordon & Jensen, 1968). A fourth paper is imminent: photo-

Table 6. *Shorter intermolecular contacts* (≤3·5 Å)

Atom in mol. 1	to	Atom	in mol.	Distance (Å)
N(1)		C(2)	2	3·23
		N(1)	2	3·48
		O(2)	2	3·32
		O(4)	4	2·83*
		H(3)	5	3·40
N(3)		O(2)	6	2·86*
		H(1)	2	3·40
O(2)		H(3)	5	1·96*
		H(*m*3)	2	2·81
		C(7)	2	3·46
		C(6)	2	3·34
		H(6)	2	2·84
		C(7)	3	3·40
		H(*m*2)	3	3·38
		H(*m*3)	3	2·70
O(4)		H(1)	7	1·93*
		H(6)	7	3·44
		H(*m*1)	8	3·32
		H(*m*2)	9	3·05
C(2)		N(1)	2	3·23
		H(1)	2	3·35
		H(3)	5	2·80
		H(6)	2	3·44
C(4)		H(1)	7	3·13
C(7)		H(6)	10	3·05
		H(*m*1)	10	3·41
		H(*m*2)	11	3·36
H(1)		H(3)	5	3·20
H(3)		H(*m*3)	12	3·38
		H(*m*3)	3	3·11
H(6)		H(*m*1)	11	2·80
		H(*m*2)	4	3·45
		H(*m*2)	11	2·92
		H(*m*3)	11	2·90
H(*m*1)		H(*m*2)	11	2·59
H(*m*2)		H(*m*3)	10	3·24

* Denotes distance between H-bonded atoms

Hydrogen bond angles

N(1)–H(1)–O(4)	165°28′
C(4)–O(4)–H(1)	170°36′
N(3)–H(3)–O(2)	167°50′
C(2)–O(2)–H(3)	121°05′

Molecule	General coordinates		
1	x	y	z
2	$1-x$	y	z
3	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
4	x	y	$-1+z$
5	x	$\frac{1}{2}-y$	$-\frac{1}{2}+z$
6	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
7	x	y	$1+z$
8	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
9	$-x$	$-y$	$1-z$
10	x	$-\frac{1}{2}-y$	$\frac{1}{2}+z$
11	x	$-\frac{1}{2}-y$	$-\frac{1}{2}+z$
12	$1-x$	$-y$	$1-z$

dimer *C* of 1,3-dimethylthymine (Camerman, Weinblum & Nyburg, 1969).

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The Structure of the Orthorhombic Amphibole Holmquistite

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A two-dimensional refinement of the structure of holmquistite has shown segregation of the cations in different sites. Iron is preferentially concentrated in the sites $M1$ and $M3$ which are internal to the chains, and lithium in the essentially inter-chain site $M4$. It is concluded that aluminum is concentrated in the site $M2$ which has both intra- and inter-chain coordinations.

1. Introduction

Holmquistite is a lithium aluminum amphibole whose ideal formula can be written as

$$Li_2Al_2(Mg,Fe)_3Si_8O_{22}(OH)_2.$$

It was shown by Vogt, Bastiansen & Skancke (1958) to be a member of the orthorhombic series of amphiboles, and it was suggested by Whittaker (1960) that this was associated with the small size of the lithium ion. More recently, Ginsburg (1965) has also found a monoclinic holmquistite.

The structure of orthorhombic holmquistite is of interest for two reasons:

(i) Very little detailed information is available on the structure of any orthorhombic amphibole. The structure of anthophyllite was determined in principle by Warren & Modell (1930), and further work was done on the same mineral by Ito (1950), but no refinement of its structure has been published. No structural study of any other orthorhombic amphibole has been reported.

(ii) In the monoclinic alkali amphiboles in which the alkali ion is sodium, this ion is confined to a single crystallographic site by its size. In magnesio-riebeckite (Whittaker, 1949) and glaucophane II (Ernst, 1963; Colville, Ernst & Gilbert, 1966; Papike & Clark, 1968) the trivalent ion [Fe^{III} and Al respectively] is also ordered to a considerable extent, and its ordering may be regarded as consequential on the effect of the confinement of the monovalent ion to a single neighbouring site. In holmquistite the primary effect of size will not lead to a marked ordering of the lithium into a particular site, and any ordering of the cations among the