Table 4 (*cont.*)

Index	Symmetry operator		
III	($-x$,	$\frac{1}{2}+y$,	$-z$)
IV	($-x$,	$\frac{1}{2}+y$,	$1-z$)
V	($1-x$,	$-\frac{1}{2}+y$,	$-z$)
VI	($1-x$,	$-\frac{1}{2}+y$,	$1-z$)
VII	(x,	$1+y$,	z)

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Crystal Structure of a Thymine–Thymine Adduct from Irradiated Thymine

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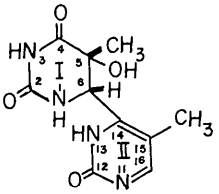
Thymine irradiated in a frozen aqueous solution with ultraviolet light produces not only dimers which are cyclobutane derivatives but also a racemic thymine–thymine adduct,

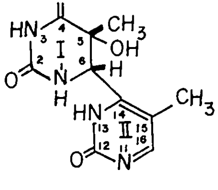


5α-hydroxy-6α-4′-[5′-methylpyrimidin-2′-one]-dihydrothymine (one of the antipodes). The material crystallizes with one molecule of H_2O in the triclinic space group $P\bar{1}$, with $Z=2$ and $a=9\cdot44\pm0\cdot02$, $b=8\cdot29\pm0\cdot02$, $c=7\cdot57\pm0\cdot02$ Å; $\alpha=99\cdot0\pm0\cdot25°$, $\beta=91\cdot5\pm0\cdot25°$ and $\gamma=89\cdot8\pm0\cdot25°$. The structure was solved by obtaining phases directly from the structure factor magnitudes with the use of the symbolic addition procedure. Ring I has the half-chair conformation while ring II is planar. The CH_3 group on C(5) and ring II on C(6) are both axial to ring I while the OH group on C(5) and the H atom on C(6) are equatorial. The dihedral angle between the planes of rings I and II is ~96°. An extensive system of hydrogen bonding between the three C=O groups, the OH, two of the NH groups and the H_2O molecule binds the molecules together in the crystal.

Introduction

Ultraviolet irradiation of frozen aqueous solutions of thymine and of deoxyribonucleic acid (DNA) has yielded cyclobutane-type dimers of thymine (Wang, 1960, 1961; Beukers, IJlstra & Berends, 1960). Of the four possible cyclobutane-type dimers (Wulff & Fraenkel, 1961; Weinblum & Johns, 1966), detailed crystal structure analyses have been performed for the *syn* 5,5:6,6 type (Camerman & Camerman, 1968; Wei & Einstein, 1968; Adman, Gordon & Jensen, 1968), for the *syn* 5,6:5,6 type (Camerman, Weinblum & Nyburg, 1968) and the anti 5,6:5,6 type (Camerman, Nyburg & Weinblum, 1967; Einstein, Hosszu, Longworth, Rahn & Wei, 1967).

A different kind of thymine–thymine product has been isolated from an ultraviolet-irradiated frozen solution of thymine (Varghese & Wang, 1968). Spectroscopic evidence supported the adduct structure:



The X-ray diffraction analysis confirmed the structural formula with the possibility that an H atom exists on N(13) rather than N(11), and established the stereoconfiguration of the molecule. This type of photoreaction may be of considerable significance in the photobiology of nucleic acids. A preliminary account of the structure has been reported (Karle, Wang & Varghese, 1968).

Experimental

One crystal of the thymine–thymine adduct was supplied by Professor S. Y. Wang of The Johns Hopkins University. The clear, colorless crystal was in the shape of a diamond plate. Multiple-film, equi-inclination Weissenberg photographs were taken with the crystal mounted along one diagonal of the diamond face and also with the crystal remounted along the other diagonal. The cell parameters, determined from precession photographs are listed in Table 1 together with other physical data. The material crystallizes in the triclinic system and the $P\bar{1}$ space group was assigned on the basis of the statistical averages of normalized structure factors and the distribution of the $|E|$ values (Table 2). Corrections were made for the Lorentz and polarization factors and for spot size but no absorption corrections were made.

Table 1. *Physical constants for 5α-hydroxy-6α-4′-[5′-methylpyrimidin-2′-one]-dihydrothymine*

Molecular formula	$C_{10}H_{12}N_4O_4.H_2O$
Mol. wt.	270·2
Melting point	265–270°C (dec.)
Habit	Tabular
Crystal size	~1·0 × 1·0 × 0·4 mm
Space group	$P\bar{1}$
a	9·44 ± 0·02 Å
b	8·29 ± 0·02
c	7·57 ± 0·02
α	99·0 ± 0·25°
β	91·5 ± 0·25
γ	89·8 ± 0·25
Z	2
V	584·6 Å^3
Density (calculated)	1·535 g.cm^{-3}
Density (flotation)	1·557 g.cm^{-3}
Radiation	Cu $K\alpha$, 1·5418 Å
Number of independent reflections	1844

Table 2. *Statistical averages and distribution*

	Experimental	Centrosymmetric	Non-centrosymmetric
$\langle\lvert E\rvert\rangle$	0·788	0·798	0·886
$\langle\lvert E^2-1\rvert\rangle$	0·992	0·968	0·736
$\lvert E\rvert > 3·0$	0·5%	0·3%	0·01%
$\lvert E\rvert > 2·0$	4·2	5·0	1·8
$\lvert E\rvert > 1·0$	26·9	32·0	37·0

Structure analysis

Phases for the reflections were obtained directly from the normalized structure factor magnitudes by the symbolic addition procedure (Karle & Karle, 1963, 1966) The three reflections used to specify the origin and six additional reflections, whose phases were designated by a symbol, which were used to implement the Σ_2 relation are listed in Table 3. In the course of the phase determination, it became apparent that $a=+$, $c=d$, $b=g=f$ and probably $c=+$. In this case, $b=-$ in order to avoid all positive signs in space group $P\bar{1}$. With this assignment of symbols, phases were determined for 346 reflections with $|E| > 1·3$. The resulting E map is shown on the left-hand side of Fig. 1 where the nineteen strongest peaks define the thymine-thymine adduct and the water of crystallization.

Table 3. *Phase assignments for specifying the origin and implementing the Σ_2 relation*

$\mathbf{h}$	$\varphi_{\mathbf{h}}$	$\lvert E\rvert$
$2\ 0\ 3$	+	3·0
$\bar{6}\ 1\ 3$	+	3·3
$3\ 5\ \bar{4}$	+	3·4
$2\ 8\ \bar{6}$	a	3·4
$0\ \bar{2}\ 2$	b	3·0
$6\ \bar{4}\ 5$	c	3·5
$4\ 5\ \bar{4}$	d	3·3
$3\ 1\ \bar{4}$	g	2·8
$2\ 5\ \bar{5}$	f	2·4

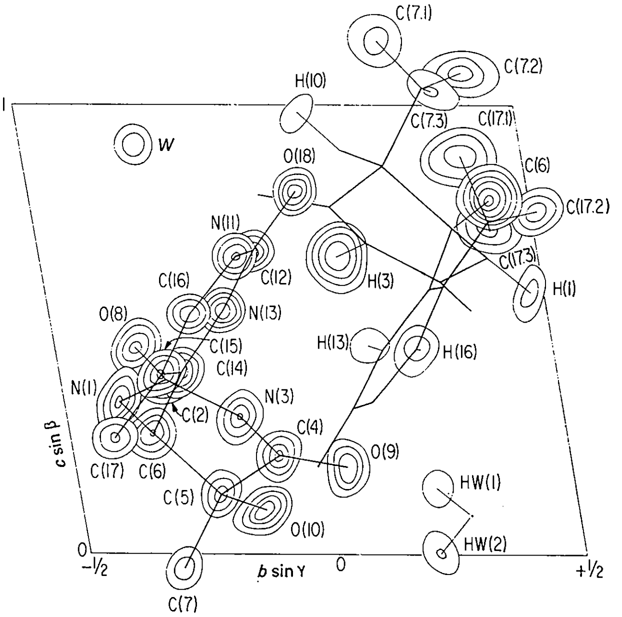


Fig. 1. Sections of a three-dimensional E map computed with 346 reflections with $|E| > 1·3$ are shown on the left side. The contours are evenly spaced on an arbitrary scale. On the right side are sections from a difference map which indicate the location of hydrogen atoms. The contours are spaced by 0·2 e.Å^{-3} beginning with the 0·3 e.Å^{-3} level.

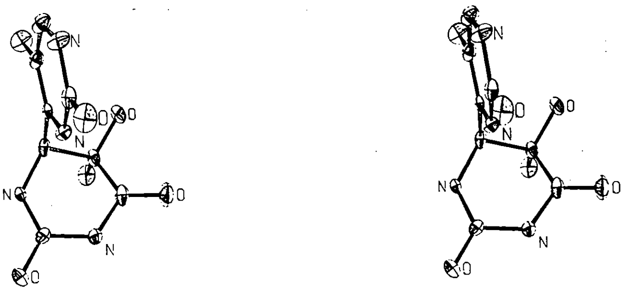


Fig. 2. A pair of stereodiagrams illustrating the configuration of the thymine–thymine adduct.

Table 4. *Observed and calculated structure factors*

The column headings are the index l, $|F_o|$ and F_c.

0	-10	L
1	4.3	-3.4
2	8.9	-7.7
3	9.0	7.8
4	7.1	-7.3
0	-9	L
1	0.0	-0.5
2	0.0	-0.9
3	9.8	-9.8
4	3.1	-2.2
5	4.8	-3.8
6	4.1	3.7
0	-8	L
1	6.4	-6.1
2	14.7	14.6
3	0.0	-0.5
4	16.3	-15.5
5	5.2	4.6
6	6.0	-4.8
7	1.3	-0.8
0	-7	L
1	5.2	4.3
2	10.9	11.1
3	8.3	8.8
4	11.8	-11.1
5	0.0	1.1
6	2.9	-3.2
7	2.4	-3.0
8	0.0	0.2
0	-6	L
1	0.0	[illegible]
2	5.9	[illegible]
3	6.1	-5.7
4	0.0	-1.1
5	2.6	-3.6
6	0.0	-0.0
7	4.3	-4.0
8	1.6	2.2
0	-5	L
1	18.6	17.6
2	3.0	-1.8
3	19.7	-17.9
4	21.6	20.2
5	5.1	-2.9
6	2.6	-1.8
7	7.5	7.0
8	7.2	-5.4
9	1.1	-1.7
0	-4	L
1	25.0	26.3
2	35.2	34.6
3	32.1	-28.3
4	25.1	23.4
5	10.3	9.1
6	8.7	-6.1
7	11.0	9.6
8	2.3	1.5
9	11.0	-13.4
0	-3	L
1	5.1	-2.4
2	30.5	-31.9
3	9.1	8.4
4	5.9	-3.7
5	11.3	8.3
6	2.6	-2.9
7	4.1	-4.0
8	9.7	9.1
9	13.9	-14.3
0	-2	L
1	43.7	51.7
2	111.9	-125.4
3	11.7	-8.0
4	2.4	1.1
5	18.5	14.6
6	10.6	8.5
7	0.0	-1.4
8	10.2	-11.1
9	11.3	11.9
0	-1	L
1	34.4	-36.1
2	0.0	2.7
3	25.4	-19.1
4	7.7	4.4
5	12.8	10.8
6	14.4	14.8
7	14.8	13.9
8	19.9	-20.9
9	13.7	13.9
0	0	L
1	29.3	-31.5
2	22.2	-16.2
3	6.2	-4.5
4	11.0	-9.3
5	6.2	-5.2
6	0.0	-0.8
7	4.3	-5.0
8	6.7	-7.2
9	9.7	9.9
0	1	L
0	42.1	40.2
1	54.6	56.5
2	41.7	-49.6
3	22.6	-22.3
4	13.7	-11.0
5	7.6	-5.8
6	15.1	13.6
7	26.2	-26.0
8	0.0	-3.1
9	6.7	7.3
0	2	L
0	35.1	-42.0
1	13.4	-12.1
2	8.8	7.5
3	0.0	-0.8
4	24.4	25.2
5	9.1	8.4
6	19.2	18.6
7	17.1	-17.2
8	5.3	-3.9
9	0.0	-1.6
0	3	L
0	25.2	25.8
1	5.0	10.0
2	15.2	14.7
3	5.4	-3.2
4	9.7	9.6
5	29.1	30.8
6	4.2	-3.3
7	6.0	-6.5
8	7.9	-7.9
0	4	L
0	16.3	-18.2
1	0.0	2.1
2	12.3	-11.6
3	13.0	-13.2
4	25.5	-27.7
5	23.0	24.9
6	4.0	-3.3
7	2.2	-1.3
8	0.0	0.1
0	5	L
0	17.2	-16.9
1	13.0	-13.0
2	10.8	-10.0
3	12.1	-12.5
4	6.4	-5.0
5	5.8	3.2
6	9.6	10.0
7	4.2	3.4
0	6	L
0	0.0	1.0
1	4.9	-1.5
2	13.6	14.8
3	6.4	-5.2
4	11.4	11.8
5	2.4	-1.9
6	2.4	-1.8
7	6.8	6.7
0	7	L
0	9.2	8.0
1	0.0	0.9
2	0.0	0.2
3	0.0	0.6
4	0.0	-2.0
5	2.4	-2.0
6	8.4	-9.0
0	8	L
0	2.6	-1.6
1	2.6	1.8
2	11.8	-10.9
3	1.6	-1.6
4	0.0	0.3
5	7.2	-6.5
0	9	L
0	1.6	-1.2
1	4.6	3.6
2	0.0	0.2
3	0.0	-0.4
0	10	L
0	2.9	1.7
1	7.1	6.7
1	-10	L
-1	9.0	-7.9
0	2.3	-2.1
1	0.0	0.5
2	5.7	4.7
3	1.9	-3.1
4	3.8	3.7
1	-9	L
-3	5.3	-4.2
-2	4.3	-3.6
-1	2.1	2.2
0	5.3	-3.6
1	7.7	6.6
2	0.0	0.9
3	0.0	1.6
4	0.0	-0.1
5	0.0	-1.2
6	9.8	9.8
1	-8	L
-5	7.4	-6.6
-4	10.9	9.6
-3	8.7	8.6
-2	18.3	-16.7
-1	0.0	-2.0
0	0.0	0.4
1	14.9	13.9
2	7.9	-8.1
3	0.0	-2.2
4	15.6	-16.4
5	3.8	3.7
6	2.3	2.2
7	4.5	4.5
1	-7	L
-6	3.7	2.9
-5	0.0	1.0
-4	0.0	1.4
-3	12.3	12.4
-2	0.0	-1.3
-1	16.1	-16.7
0	1.8	1.6
1	6.6	5.7
2	0.0	1.6
3	5.7	-4.9
4	13.5	-13.7
5	4.3	-4.9
6	17.0	18.7
7	8.2	9.1
8	7.1	-8.7
1	-6	L
-7	3.9	-3.9
-6	8.1	-7.3
-5	0.0	1.6
-4	18.4	17.8
-3	3.6	4.0
-2	1.7	2.1
-1	20.9	-21.3
0	17.6	17.9
1	0.0	-0.9
2	8.4	8.1
3	0.0	-1.3
4	8.8	-6.8
5	0.0	-2.3
6	7.4	7.1
7	12.1	14.0
8	11.4	-11.9
1	-5	L
-7	3.7	2.9
-6	0.0	-1.7
-5	14.8	-14.6
-4	0.0	-0.2
-3	11.2	10.1
-2	7.2	-5.7
-1	13.9	-13.8
0	13.8	12.0
1	27.6	27.6
2	4.2	-4.3
3	4.7	-4.9
4	24.6	-23.0
5	7.0	-5.5
6	7.6	7.0
7	4.4	-4.9
8	0.0	-1.5
9	5.2	-6.5
1	-4	L
-8	0.0	0.6
-7	5.6	-4.8
-6	6.5	-7.0
-5	2.5	-3.3
-4	11.7	-10.2
-3	6.6	-6.5
-2	10.7	-11.6
-1	14.5	13.3
0	0.0	0.3
1	25.4	22.4
2	25.7	23.9
3	36.4	-31.2
4	16.5	-14.9
5	14.7	-13.4
6	14.5	13.0
7	2.5	-1.6
8	7.4	6.6
9	0.0	-0.6
1	-3	L
-8	3.5	2.3
-7	6.6	6.4
-6	0.0	0.0
-5	7.8	7.2
-4	18.3	18.4
-3	11.9	-10.2
-2	32.1	-31.6
-1	3.9	-2.3
0	10.4	9.5
1	16.1	-14.1
2	55.5	55.9
3	7.0	-6.0
4	18.3	-14.9
5	19.3	17.5
6	0.0	1.3
7	0.0	-2.2
8	3.2	2.0
9	0.0	-0.1
1	-2	L
-9	2.3	-2.7
-8	0.0	-0.7
-7	11.0	11.7
-6	0.0	-0.3
-5	23.5	22.9
-4	16.2	15.9
-3	17.9	-16.3
-2	32.7	-34.0
-1	15.7	-13.0
0	23.0	-23.9
1	3.7	-1.0
2	16.0	12.8
3	32.6	20.2
4	10.2	-8.5
5	16.7	13.8
6	6.0	-3.9
7	12.6	-10.5
8	2.3	-2.6
9	11.3	-11.6
1	-1	L
-9	1.3	0.9
-8	8.3	-8.9
-7	0.0	0.7
-6	16.7	-16.3
-5	5.0	2.9
-4	26.3	22.1
-3	16.4	-14.3
-2	30.5	-29.7
-1	27.7	28.5
0	36.3	-44.4
1	6.7	7.1
2	8.8	-8.3
3	37.2	-29.6
4	13.5	11.5
5	15.7	15.3
6	3.4	3.5
7	8.7	-8.2
8	11.5	11.4
9	11.7	-12.2
1	0	L
-9	4.2	-4.5
-8	4.1	3.0
-7	26.6	-25.6
-6	5.2	4.1
-5	0.0	-0.7
-4	15.1	12.9
-3	21.9	16.9
-2	25.5	21.3
-1	40.4	42.4
0	8.1	9.6
1	17.6	-14.2
2	37.0	-35.4
3	16.1	-14.7
4	10.6	-9.4
5	15.3	14.1
6	14.8	13.8
7	16.1	15.6
8	0.0	-0.3
9	0.0	-1.3
1	1	L
-9	6.5	-6.4
-8	19.6	20.5
-7	11.4	-10.4
-6	6.9	-3.1
-5	23.8	20.9
-4	0.0	0.2
-3	0.0	-1.9
-2	30.0	25.1
-1	24.2	-22.8
0	26.3	28.6
1	43.1	47.4
2	62.9	-75.8
3	24.7	-22.4
4	12.2	11.8
5	3.9	-4.1
6	18.4	-17.7
7	26.8	25.8
8	6.9	-6.9
9	1.8	-1.3
1	2	L
-8	5.7	-5.2
-7	0.0	2.4
-6	6.0	-5.3
-5	7.3	-6.3
-4	26.7	-22.5
-3	32.7	-29.8
-2	40.6	34.8
0	18.9	19.2
1	32.3	34.3
2	29.9	29.7
3	31.6	-31.9
4	8.2	2.6
5	3.7	-4.2
6	13.5	-13.9
7	0.0	0.3
8	1.8	-0.5
9	2.2	2.5
1	3	L
-9	17.5	17.9
-8	3.2	2.9
-7	22.1	-21.6
-6	3.9	-3.4
-5	6.0	-4.1
-4	9.8	-7.2
-3	7.3	-6.0
-1	15.5	-13.8
0	33.6	31.9
1	9.4	8.3
2	12.5	10.1
3	14.1	13.3
4	5.9	5.3
5	20.8	-24.4
6	12.3	11.6
7	1.6	-2.3
8	2.2	-2.7
1	4	L
-9	2.7	-3.5
-8	14.2	15.7
-2	17.1	-17.7
-1	7.7	7.2
0	24.7	-23.7
1	13.0	14.0
2	5.7	-5.9
3	2.2	-1.7
4	15.1	15.1
5	9.3	-9.3
6	6.5	6.3
7	3.6	-2.9
8	4.1	-3.9
1	5	L
-9	5.7	7.2
-8	0.0	-0.0
-7	21.5	22.5
-6	4.0	4.1
-5	9.7	-8.3
-4	22.9	-22.4
-3	19.8	18.9
-2	19.5	-19.1
-1	6.5	-5.5
0	18.5	-18.4
1	18.0	-18.5
2	18.6	17.8
3	15.9	16.2
4	16.0	-16.5
5	3.9	3.6
6	8.5	8.5
7	2.6	-1.2
1	6	L
-8	2.1	2.7
-7	2.7	3.6
-6	7.4	6.6
-5	27.1	-26.4
-4	14.8	13.1
-3	3.8	-3.2
-2	4.0	3.3
-1	6.5	-5.8
0	3.7	2.7
1	7.3	-6.7
2	0.0	-1.3
3	28.4	30.8
4	13.6	-14.9
5	3.6	-3.7
6	0.0	1.6
7	6.5	6.8
1	7	L
-8	5.5	-5.5
-7	6.6	5.3
-6	11.3	11.8
-5	22.1	-21.5
-4	19.1	18.5
-3	21.3	21.7
-2	7.1	6.3
-1	1.8	2.2
0	13.7	-13.2
1	4.4	-4.2
2	4.0	3.9
3	5.5	5.4
4	5.0	-4.7
5	0.0	-2.5
6	0.0	-0.4
1	8	L
-7	2.1	2.0
-6	0.0	-1.6
-5	2.2	0.6
-4	4.1	-4.2
-3	13.1	13.7
-2	11.2	10.8
-1	6.1	-5.1
0	10.2	-9.5
1	20.6	-20.4
2	10.6	10.5
3	2.1	-2.1
4	0.0	1.2
5	4.9	-4.2
1	9	L
-6	16.9	-18.5
-5	6.4	-5.0
-4	3.9	-3.2
-3	7.7	-7.6
-2	12.8	12.5
-1	3.1	2.4
0	4.1	-3.3
1	2.9	-3.5
2	8.0	6.8
3	1.3	-1.1
1	10	L
-4	2.3	-2.1
-3	0.0	-0.6
-2	2.5	3.1
-1	12.0	10.5
0	1.9	-2.2
1	6.7	6.2
2	-10	L
-1	9.5	-8.4
0	4.4	3.3
1	5.1	-3.9
2	9.0	7.8
2	-9	L
-3	5.3	-4.8
-2	12.9	11.6
-1	9.2	-6.7
0	4.3	3.6
1	8.1	7.7
2	8.5	7.9
3	0.0	-1.2
4	0.0	-0.8
5	0.0	-0.0
2	-8	L
-4	7.0	6.2
-3	3.6	3.8
-2	9.8	-8.7
-1	9.6	8.7
0	0.0	-2.1
1	3.1	-2.3
2	7.9	7.8
3	6.9	-6.2
4	5.2	-5.3
5	7.4	-7.6
6	7.7	6.5
7	1.9	-1.9
2	-7	L
-5	1.6	1.8
-4	6.3	-6.4
-3	14.6	14.1
-2	20.5	-21.9
-1	19.4	-19.4
0	4.4	3.3
1	3.6	3.6
2	0.0	-0.3
3	0.0	0.1
4	4.4	3.8
5	6.0	-4.6
6	10.0	11.5
7	4.1	-3.3
2	-6	L
-6	0.0	0.2
-5	0.0	1.6
-4	2.5	-1.7
-3	0.0	0.8
-2	6.2	5.9
-1	12.5	-11.5
0	16.8	-17.7
1	26.6	27.0
2	4.2	4.0
3	10.5	10.4
4	5.4	-4.5
5	9.7	8.8
6	0.0	2.3
7	6.8	7.8
8	7.7	-8.4
2	-5	L
-7	7.6	-6.8
-6	0.0	-0.3
-5	6.1	-5.0
-4	16.4	17.0
-3	13.8	12.8
-2	6.6	7.2
-1	13.6	12.7
0	11.5	-12.0
1	4.7	1.9
2	15.6	-15.3
3	2.8	2.0
4	9.6	-8.7
5	0.0	-0.5
6	6.7	-7.7
7	15.0	15.3
8	7.4	-7.4
2	-4	L
-8	3.6	3.2
-7	0.0	-0.0
-6	0.0	0.5
-5	9.5	-8.4
-4	6.0	-4.0
-3	9.4	9.4
-2	31.7	33.1
-1	28.3	-30.3
0	2.3	2.9
1	17.0	-17.0
2	10.1	-8.1
3	37.5	-36.5
4	4.2	5.6
5	5.2	4.5
6	2.6	-2.5
7	13.3	14.0
8	4.4	5.2
9	1.2	0.5
2	-3	L
-8	0.0	-0.0
-7	4.0	3.8
-6	0.0	-1.2
-5	6.6	-6.1
-4	15.4	-16.0
-3	30.2	-33.8
-2	28.6	31.3
-1	13.9	14.7
0	5.8	6.5
1	4.5	-3.4
2	30.6	29.4
3	7.0	7.0
4	13.9	-10.7
5	5.0	-4.2
6	10.8	9.5
7	1.8	2.9
8	8.0	8.7
9	4.1	3.6
2	-2	L
-8	1.7	2.4
-7	13.2	12.5
-6	0.0	-0.1
-5	5.9	-5.3
-4	22.3	-23.3
-3	9.1	6.0
-2	25.1	-27.3
-1	44.0	56.5
0	35.1	38.3
1	18.8	16.8
2	1.8	-2.7
3	31.9	27.5
4	12.5	9.9
5	45.2	-42.5
6	3.1	-3.9
7	11.5	-11.5
8	0.0	-0.9
9	7.7	8.7
2	-1	L
-9	5.0	-4.9
-8	9.0	-8.9
-7	12.0	12.4
-6	14.1	13.2
-5	0.0	1.2
-4	25.3	-23.5
-3	14.9	12.5
-2	7.0	-6.9
-1	0.0	0.9
0	8.4	-10.4
1	49.5	-54.6
2	0.0	-0.8
3	3.7	3.6
4	15.9	12.3
5	11.4	-9.5
6	16.2	-15.3
7	7.2	-6.0
8	3.9	-3.4
9	6.4	6.7
2	0	L
-9	0.0	-0.8
-8	6.3	-6.9
-7	2.6	2.2
-6	21.3	20.3
-5	10.6	-8.8
-4	4.8	-5.0
-3	18.3	-15.2
-2	21.5	-15.7
-1	13.1	-8.4
0	7.4	6.3
1	71.4	-77.0
2	32.6	-31.6
3	67.0	78.4
4	5.8	5.1
5	26.8	26.2
6	2.3	2.7
7	10.4	-10.4
8	5.2	5.3
9	0.0	0.5
2	1	L
-9	3.3	-3.9
-8	0.0	0.4
-7	9.2	8.5
-6	15.1	12.8
-5	7.1	-5.1
-4	19.9	-15.7
-3	2.0	-1.2
-2	10.4	9.3
-1	37.8	36.9
0	7.8	-8.8
1	16.6	15.4
2	41.6	-44.3
3	32.0	32.2
4	29.0	27.4
5	6.6	-5.2
6	7.2	7.5
7	12.3	-11.7
8	1.5	-0.8
9	0.0	1.5
2	2	L
-9	7.3	-7.5
-8	0.0	-2.8
-7	8.8	7.5
-6	4.3	4.2
-5	3.2	-2.7
-4	1.4	0.5
-3	2.1	-4.3
-2	16.9	14.4
-1	49.9	56.5
0	14.9	-14.2
1	41.6	-44.5
2	6.0	7.0
3	44.1	-45.0
4	10.2	9.9
5	3.8	2.6
6	18.7	-19.2
7	4.9	4.1
8	9.1	7.9
2	3	L
-9	12.5	-13.3
-8	0.0	0.9
-7	6.7	-5.4
-6	0.0	0.9
-5	0.0	-0.1
-4	0.0	-0.4
-3	11.1	-8.7
-2	31.4	31.2
-1	3.8	-1.8
0	10.7	-8.2
1	33.0	-37.1
2	2.6	-0.9
3	2.1	1.2
4	14.8	-15.6
5	26.3	27.2
6	12.8	-12.5
7	1.6	0.4
8	12.4	12.6
2	4	L
-9	6.0	-7.3
-8	5.7	5.8
-7	6.6	6.9
-6	23.0	-21.0
-5	4.9	4.0
-4	9.5	6.2
-3	29.7	-27.5
-2	35.1	33.5
-1	17.0	16.6
0	26.3	-28.9
1	9.8	7.1
2	1.5	1.9
3	13.7	12.2
4	9.9	9.4
5	0.0	-0.8
6	3.9	-3.3
7	5.0	-4.8
8	2.1	2.3
2	5	L
-9	5.1	6.2
-8	5.9	5.0
-7	14.3	12.8
-6	10.8	-9.5
-5	27.8	-27.0
-4	0.0	-0.7
-3	3.2	-1.4
-2	12.9	11.2
-1	21.2	20.3
0	0.0	-0.6
1	5.0	-4.1
2	13.7	14.5
3	17.4	-19.5
4	14.6	14.4
5	12.2	-12.2
6	8.8	-9.3
7	5.6	-5.6
2	6	L
-8	13.0	13.0
-7	0.0	-0.7
-6	3.0	2.8
-5	2.6	-2.1
-4	33.5	-34.0
-3	15.7	15.0
-2	9.5	8.8
-1	2.9	-2.8
0	0.0	-2.3
1	6.0	-5.7
2	6.2	5.6
3	4.1	-4.0
4	2.5	-1.7
5	5.5	-4.8
6	0.0	0.9
2	7	L
-8	3.9	4.3
-7	15.5	15.6
-6	5.0	-3.9
-5	13.2	12.8
-4	14.2	-14.4
-3	3.1	3.6
-2	0.0	-1.7
-1	9.1	-8.3
0	6.8	-6.5
1	5.4	5.8
2	7.2	-7.1
3	20.6	22.2
4	5.0	4.6
5	5.4	-4.3
6	1.5	-1.8
2	8	L
-7	2.6	1.9
-6	23.1	21.9
-5	11.0	-11.6
-4	0.0	1.5
-3	8.5	7.0
-2	4.7	4.3
-1	13.5	-14.4
0	9.2	-7.8
1	11.9	11.2
2	6.5	-7.6
3	14.1	11.7
4	5.9	4.7
2	9	L
-6	13.8	13.8
-5	3.6	-3.7
-4	2.4	-1.8
-3	4.7	4.3
-2	9.9	9.4
-1	0.0	0.7
0	10.5	-9.4
1	10.4	-8.4
2	0.0	-0.8
3	0.0	0.8
2	10	L
-3	5.6	6.2
-2	0.0	1.4
-1	0.0	2.2
0	10.3	9.6
1	15.6	-15.5
3	-10	L
0	0.0	1.0
1	4.2	-4.5
3	-9	L
-2	2.0	2.3
-1	7.0	5.2
0	1.8	-1.3
1	1.5	-0.1
2	2.5	-1.8
3	2.4	-2.2
4	0.0	-0.3
5	6.2	6.4
3	-8	L
-4	8.8	7.5
-3	6.5	-5.2
-2	0.0	-2.3
-1	10.4	10.4
0	4.6	4.9
1	6.1	-4.9
2	0.0	0.0
3	7.6	-7.9
4	4.2	-4.4
5	12.2	10.6
6	4.4	-4.1
3	-7	L
-5	6.0	-4.8
-4	4.0	-3.9
-3	11.2	-10.8
-2	4.4	-3.9
-1	7.7	-6.7
0	21.3	23.9
1	0.0	-1.5
2	6.3	-5.7
3	6.3	-5.4
4	4.0	-4.2
5	2.4	-2.3
6	2.1	2.8
7	5.0	-5.2
3	-6	L
-6	0.0	-0.7
-5	2.7	4.1
-4	7.9	-7.8
-3	10.1	-10.9
-2	0.0	-2.0
-1	3.1	-2.9
0	11.5	12.2
1	24.2	25.4
2	9.1	-8.0
3	11.4	-9.8
4	14.9	14.9
5	3.6	-4.3
6	0.0	-0.1
7	0.0	-2.6
8	0.0	-2.4
3	-5	L
-7	3.8	3.9
-6	6.4	6.3
-5	17.2	18.2
-4	4.1	-4.1
-3	8.7	8.8
-2	13.7	-13.2
-1	6.9	6.5
0	10.4	-11.2
1	5.4	6.0
2	6.0	5.1
3	11.0	-10.9
4	15.4	14.7
5	7.3	6.6
6	4.4	4.8
7	11.4	-13.3
8	4.6	-5.0
3	-4	L
-8	2.8	3.1
-7	3.0	-2.1
-6	6.8	6.7
-5	13.8	15.3
-4	6.2	-4.3
-3	5.8	-5.8
-2	9.2	-8.7
-1	10.2	-8.1
0	4.8	-5.0
1	17.7	-16.9
2	21.1	-17.9
3	10.1	8.8
4	10.3	9.8
5	13.5	13.3
6	0.0	-0.6
7	3.4	-2.1
8	7.3	-7.0
9	8.8	-10.1
3	-3	L
-8	0.0	-1.1
-7	4.8	-4.4
-6	3.6	3.6
-5	12.9	-13.5
-4	0.0	1.9
-3	16.5	-17.6
-2	12.1	11.7
-1	23.4	22.9
0	7.0	-4.2
1	13.9	13.1
2	37.3	-34.4
3	0.0	-0.7
4	11.9	-9.3
5	37.3	36.3
6	6.3	-4.8
7	4.3	3.1
8	3.7	3.6
9	2.4	2.7
3	-2	L
-8	10.2	-10.0
-7	5.4	-4.9
-6	12.9	12.6
-5	0.0	-1.5
-4	1.6	0.1
-3	9.9	-8.8
-2	26.1	28.8
-1	45.7	57.6
0	19.2	19.3
1	35.7	-36.4
2	7.2	-6.9
3	10.4	-10.6
4	18.7	-16.5
5	0.0	0.4
6	15.1	13.1
7	5.0	3.1
8	0.0	-1.6
9	7.6	8.6
3	-1	L
-9	0.0	-1.5
-8	3.6	-4.0
-7	9.8	9.9
-6	8.8	7.0
-5	6.8	5.8
-4	8.1	6.4
-3	31.3	-28.1
-2	5.6	6.1
-1	3.1	5.0
0	46.5	55.5
1	48.4	-53.6
2	17.7	-13.1
3	21.3	-19.0
4	28.7	27.0
5	23.4	-19.5
6	14.8	-13.8
7	3.1	3.4
8	0.0	2.0
9	3.1	4.2
3	0	L
-9	0.0	1.1
-8	14.1	-14.8
-7	5.3	5.0
-6	9.4	8.9
-5	3.3	-4.2
-4	40.9	-38.6
-3	11.2	-7.9
-2	17.6	-15.4
-1	7.7	4.8
0	10.0	9.0
1	8.1	9.0
2	10.5	8.2
3	7.2	6.0
4	20.1	18.0
5	4.2	5.3
6	10.7	-10.5
7	14.2	-14.1
8	4.5	4.5
9	4.3	4.7
3	1	L
-9	7.0	6.8
-8	5.9	-6.2
-7	8.8	-8.6
-6	6.7	-5.3
-5	28.5	25.0
-4	47.4	-42.1
-3	4.2	-2.9
-2	16.4	14.4
-1	43.0	47.3
0	20.7	23.0
1	17.0	19.5
2	27.8	-30.4
3	25.7	24.6
4	22.8	21.4
5	12.9	-11.9
6	0.0	1.4
7	7.0	-6.8
8	6.6	-5.8
9	3.5	-3.5
3	2	L
-9	0.0	-0.1
-8	5.5	5.7
-7	4.0	5.3
-6	17.2	14.8
-5	4.1	3.8
-4	13.1	11.6
-3	23.2	-19.5
-2	8.2	7.2
-1	5.8	5.0

Table 4 (*cont.*)

0	6.4	-7.0
1	8.9	9.7
2	36.6	-39.1
3	13.5	-13.8
4	18.2	19.5
5	7.9	7.6
6	10.1	-10.1
7	0.0	-0.2
8	4.5	-4.0
3	3	L
-9	0.0	-0.6
-8	4.9	5.3
-7	10.7	-9.5
-6	30.9	28.8
-5	0.0	-1.0
-4	9.2	-8.5
-3	13.6	-12.2
-2	27.4	-27.5
-1	12.8	-11.3
0	16.4	-15.4
1	7.5	-7.7
2	5.5	-4.6
3	9.8	9.6
4	2.4	-2.0
5	15.8	16.6
6	4.7	4.0
7	3.5	-4.2
8	4.6	-3.4
3	4	L
-9	5.7	-6.9
-8	3.1	-3.1
-7	3.5	-4.3
-6	16.5	-15.4
-5	19.8	18.2
-4	2.9	2.2
-3	0.0	0.1
-2	5.7	-3.7
-1	3.9	-3.4
0	15.4	16.3
1	5.0	-4.7
2	6.6	6.6
3	6.7	6.4
4	2.5	3.2
5	1.8	2.0
6	6.3	5.7
7	1.6	-2.3
3	5	L
-8	15.3	-16.3
-7	8.0	7.5
-6	11.4	-10.6
-5	11.5	-11.2
-4	42.2	41.2
-3	11.4	9.6
-2	10.1	9.0
-1	1.6	1.0
0	7.0	8.2
1	15.6	-17.1
2	0.0	-0.0
3	7.6	-7.3
4	11.3	-11.7
5	6.5	6.4
6	2.6	2.7
7	6.1	-4.4
3	6	L
-7	7.2	-8.2
-6	3.0	3.5
-5	20.3	-19.6
-4	8.8	9.1
-3	17.0	16.7
-2	11.1	-10.5
-1	1.7	1.0
0	4.3	-4.0
1	6.6	-5.5
2	9.2	-9.2
3	3.1	-3.8
4	8.7	-9.0
5	3.1	3.8
6	10.2	9.7
3	7	L
-7	0.0	2.0
-6	15.0	-16.4
-5	0.0	-2.3
-4	13.5	-13.9
-3	0.0	0.8
-2	5.5	-5.6
-1	0.0	2.2
0	3.6	3.7
1	9.5	9.5
2	15.0	15.8
3	8.8	-9.2
4	1.5	-1.1
5	0.0	-1.2
3	8	L
-6	7.9	-8.4
-5	0.0	1.3
-4	3.2	2.3
-3	3.4	-3.8
-2	0.0	1.7
-1	0.0	-2.9
0	10.3	9.3
1	6.7	6.0
2	11.6	11.4
3	3.4	-2.6
4	5.7	-5.2
3	9	L
-5	7.9	8.0
-4	0.0	2.1
-3	0.0	-0.8
-2	0.0	0.8
-1	9.4	-10.1
0	17.4	-15.1
1	14.6	12.4
2	4.0	-3.9
3	2.3	-1.7
3	10	L
-3	5.5	-4.7
-2	4.2	-3.8
-1	3.0	2.5
0	15.1	-15.0
4	-9	L
-2	10.8	-10.5
-1	6.3	-5.9
0	0.0	0.8
1	12.2	11.3
2	17.7	-18.7
3	11.7	11.5
4	1.6	2.1
4	-8	L
-4	4.4	3.8
-3	4.6	3.9
-2	8.9	-9.1
-1	5.8	5.5
0	2.0	1.8
1	2.9	-0.8
2	4.9	5.2
3	8.3	-9.7
4	6.6	7.7
5	4.7	4.7
6	6.6	7.6
4	-7	L
-5	2.7	2.8
-4	7.3	5.7
-3	5.2	5.5
-2	7.3	-7.4
-1	0.0	-0.8
0	27.4	31.7
1	19.4	-21.6
2	8.7	-8.9
3	5.2	-4.7
4	12.9	-14.3
5	7.2	8.1
6	4.9	5.1
7	0.0	0.6
4	-6	L
-6	6.3	-5.6
-5	3.7	-2.4
-4	3.8	4.1
-3	3.7	-4.1
-2	0.0	0.3
-1	8.1	-8.1
0	12.4	12.8
1	17.6	19.0
2	24.3	-27.9
3	7.9	-8.2
4	7.9	-7.6
5	5.9	5.6
6	7.7	9.0
7	0.0	0.7
4	-5	L
-7	0.0	-0.4
-6	2.5	2.0
-5	0.0	-1.2
-4	4.0	6.1
-3	13.4	-14.3
-2	12.8	-14.0
-1	15.6	14.5
0	0.0	-0.6
1	20.2	20.4
2	20.6	21.3
3	20.8	-22.2
4	5.3	4.1
5	2.2	2.2
6	1.5	1.9
7	6.8	-7.5
8	0.0	1.8
4	-4	L
-7	3.7	-3.3
-6	2.4	-3.1
-5	5.7	5.8
-4	0.0	0.3
-3	5.0	-4.4
-2	12.7	-13.0
-1	7.2	-7.2
0	15.1	16.5
1	0.0	0.7
2	26.6	25.3
3	12.5	-11.8
4	5.5	-4.3
5	2.6	1.8
6	9.5	-9.2
7	8.6	-9.8
8	8.6	-9.7
4	-3	L
-8	1.5	1.6
-7	5.1	5.5
-6	16.8	-17.3
-5	12.7	13.4
-4	0.0	0.1
-3	7.2	-6.0
-2	5.5	3.6
-1	3.2	-2.2
0	27.1	-26.3
1	8.2	7.3
2	7.8	-6.5
3	1.3	-1.9
4	2.8	-1.1
4	-2	L
-8	3.1	-3.0
-7	8.4	8.2
-6	2.6	-2.4
-5	0.0	0.3
-4	9.8	8.4
-3	7.9	4.9
-2	11.5	-12.4
-1	8.8	8.2
0	24.3	-26.3
1	2.3	-3.1
2	1.5	-1.6
3	4.1	3.8
4	9.7	9.4
5	13.0	11.6
6	15.5	18.3
7	2.3	-1.0
8	1.5	1.6
4	-1	L
-8	12.6	11.5
-7	7.7	-7.2
-6	17.4	16.8
-5	7.8	-6.7
-4	0.0	0.3
-3	3.0	2.0
-2	12.3	12.9
-1	8.6	-5.8
0	5.2	-4.9
1	1.4	-1.6
2	4.9	-3.1
3	19.6	17.8
4	15.3	-11.9
5	5.4	-3.8
6	1.5	0.8
7	13.9	14.4
8	11.9	-11.1
4	0	L
-9	7.3	-7.7
-8	4.4	3.0
-7	8.6	-8.7
-6	0.0	0.4
-5	8.9	-8.1
-4	6.6	5.5
-3	13.6	11.5
-2	7.8	6.4
-1	2.8	-1.0
0	11.1	8.1
1	8.6	-8.9
2	25.1	-23.1
3	7.5	6.9
4	14.8	-12.5
5	8.2	-9.0
6	11.4	-12.8
7	12.8	12.6
8	7.4	7.7
4	1	L
-9	6.8	6.8
-8	14.9	-16.2
-7	4.2	-3.9
-6	3.8	-3.7
-5	2.5	-2.4
-4	7.2	-7.2
-3	24.4	22.3
-2	38.0	37.3
-1	35.2	-38.4
0	7.4	6.6
1	12.2	-13.7
2	10.2	9.4
3	10.7	-11.0
4	9.2	9.0
5	8.2	-7.8
6	8.5	8.7
7	0.0	-0.3
8	2.3	3.2
4	2	L
-9	14.4	16.7
-8	2.8	3.9
-7	5.6	-3.0
-6	10.8	-10.6
-5	2.0	2.7
-4	0.0	0.9
-3	15.5	-13.1
-2	26.7	25.1
-1	10.7	11.6
0	7.7	-8.6
1	6.9	-7.7
2	19.8	21.2
3	7.0	-5.8
4	10.3	10.0
5	9.3	-9.9
6	3.4	-3.2
7	1.9	3.3
8	3.1	-3.0
4	3	L
-9	5.6	7.6
-8	14.2	14.1
-7	6.5	6.8
-6	17.4	-15.8
-5	10.1	-10.5
-4	15.5	-14.6
-3	17.2	15.0
-2	28.7	-29.8
-1	18.6	20.0
0	0.0	-1.4
1	18.1	20.0
2	4.6	4.6
3	1.9	-0.9
4	9.7	-10.5
5	0.0	0.2
6	7.6	-8.7
7	9.7	-8.8
4	4	L
-8	6.2	6.9
-7	0.0	-0.9
-6	6.5	-6.6
-5	7.6	6.5
-4	9.8	-7.4
-3	3.6	2.8
-2	2.5	-0.2
-1	9.2	-8.6
0	15.6	-16.5
1	20.6	22.8
2	7.3	8.3
3	3.9	4.4
4	6.9	-7.8
5	2.1	-3.0
6	7.0	7.9
4	5	L
-8	8.4	9.5
-7	1.9	-1.4
-6	3.0	3.0
-5	2.2	-0.9
-4	37.4	38.2
-3	7.0	-5.8
-2	12.9	-11.6
-1	11.9	-12.5
0	13.3	-13.2
1	3.2	-0.7
2	10.5	11.8
3	7.9	8.4
4	2.6	3.0
5	1.4	2.3
6	6.0	-4.8
4	6	L
-7	1.4	-2.0
-6	2.0	2.3
-5	10.2	-9.7
-4	10.5	9.8
-3	25.7	25.8
-2	10.6	-10.9
-1	25.8	-28.4
0	2.1	2.9
1	2.6	-2.8
2	1.5	0.8
3	5.2	5.0
4	4.0	-4.5
5	5.1	4.7
4	7	L
-7	4.5	-5.8
-6	15.7	-14.2
-5	0.0	-2.4
-4	0.0	-1.4
-3	9.9	11.2
-2	16.3	17.7
-1	15.1	-15.2
0	0.0	0.4
1	2.1	2.9
2	3.3	-3.8
3	3.0	-3.1
5	5.9	-5.6
4	8	L
-6	3.6	-3.1
-5	10.7	-10.6
-4	9.1	10.1
-3	8.4	9.8
-2	0.0	1.0
-1	4.0	4.3
0	0.0	-0.7
1	3.8	3.5
2	3.4	2.8
3	6.5	-5.8
4	9	L
-4	8.2	-7.9
-3	11.6	10.6
-2	8.9	-7.7
-1	5.3	-4.2
0	0.0	1.0
1	1.8	1.7
2	6.5	7.2
5	-9	L
-2	5.6	-4.9
-1	3.9	2.7
0	1.7	2.1
1	3.0	-2.4
2	6.3	6.3
3	1.6	1.7
4	3.3	-2.6
5	-8	L
-3	3.9	-2.7
-2	4.7	-3.4
-1	0.0	1.3
0	0.0	-2.2
1	11.3	12.9
2	3.4	-3.8
3	2.8	2.5
4	12.6	12.2
5	0.0	-0.4
5	-7	L
-4	3.4	1.8
-3	6.1	6.8
-2	1.9	1.9
-1	0.0	0.2
0	11.0	-11.3
1	3.3	3.8
2	10.2	-10.5
3	5.7	5.4
4	1.4	1.6
5	8.8	7.6
6	1.2	-1.9
5	-6	L
-5	7.8	7.0
-4	5.6	-6.4
-3	2.0	1.3
-2	0.0	2.0
-1	9.7	-9.6
0	0.0	0.9
1	3.9	-3.0
2	21.8	-23.9
3	2.6	3.8
4	13.5	13.8
5	4.2	-3.8
6	2.1	1.1
7	14.5	17.0
5	-5	L
-6	6.6	-5.4
-5	9.2	-9.0
-4	5.0	-4.0
-3	1.5	-0.4
-2	16.8	17.9
-1	14.9	-13.5
0	16.0	17.0
1	4.2	2.8
2	0.0	-0.8
3	16.3	-17.3
4	9.7	10.4
5	6.6	5.5
6	4.7	-4.8
7	10.9	10.7
8	4.2	4.0
5	-4	L
-7	4.5	-4.8
-6	8.8	8.9
-5	5.8	-5.8
-4	2.6	-1.4
-3	6.2	6.1
-2	17.1	18.6
-1	5.9	5.9
0	6.8	6.4
1	5.4	-5.0
2	0.0	0.6
3	7.4	5.8
4	19.3	-20.8
5	8.4	-8.2
6	8.7	7.9
7	7.5	-9.0
8	4.1	3.7
5	-3	L
-7	5.5	5.3
-6	7.2	-6.2
-5	3.0	-2.3
-4	2.6	-2.8
-3	13.3	13.2
-2	14.9	-14.1
-1	8.0	9.5
0	15.6	-15.8
1	6.0	-6.7
2	4.8	-2.0
3	12.1	11.0
4	2.8	2.7
5	20.8	-19.9
6	3.6	3.7
7	5.9	-6.4
8	0.0	-0.1
5	-2	L
-8	4.3	-4.3
-7	15.4	17.7
-6	6.5	-6.1
-5	23.3	-24.1
-4	11.6	-11.4
-3	10.0	8.7
-2	5.1	-5.2
-1	5.4	2.8
0	0.0	-2.8
1	25.3	-24.9
2	35.9	39.7
3	11.9	10.7
4	1.9	1.8
5	3.9	3.6
6	1.5	-1.0
7	4.1	-4.2
8	0.0	-0.4
5	-1	L
-8	0.0	2.1
-7	9.1	9.5
-6	3.9	2.3
-5	19.3	-20.6
-4	5.1	-5.2
-3	2.4	2.8
-2	16.6	17.6
-1	11.4	11.0
0	4.8	4.6
1	14.3	-13.4
2	10.0	9.7
3	32.5	31.9
4	17.7	-15.5
5	2.5	-2.5
6	2.1	-2.5
7	1.9	-2.0
8	0.0	-0.2
5	0	L
-8	6.6	6.1
-7	17.4	18.8
-6	7.1	6.0
-5	7.0	-5.6
-4	1.3	-2.0
-3	11.5	12.1
-2	0.0	0.3
-1	13.9	10.9
0	49.9	-48.8
1	7.5	-6.4
2	9.0	-7.1
3	13.0	10.7
4	0.0	-0.5
5	13.2	-10.9
6	2.7	-3.2
7	0.0	0.7
8	8.9	9.4
5	1	L
-8	0.0	0.4
-7	6.3	6.0
-6	10.2	9.2
-5	2.0	-1.8
-4	9.2	-8.3
-3	3.0	2.2
-2	5.1	4.3
-1	21.2	-20.1
0	25.2	-31.8
1	18.8	-20.5
2	11.0	10.9
3	13.1	13.1
4	15.7	16.3
5	0.0	-0.9
6	5.9	-5.9
7	7.3	7.4
8	6.8	7.6
5	2	L
-8	3.4	4.4
-7	9.8	-9.3
-6	0.0	-2.0
-5	2.5	-3.7
-4	2.3	2.0
-3	5.9	-3.5
-2	41.3	45.9
-1	3.9	-2.5
0	18.0	-21.2
1	3.9	4.8
2	7.1	7.5
3	8.3	7.4
4	7.4	7.0
5	4.0	6.1
6	13.5	-15.0
7	7.6	6.6
5	3	L
-8	0.0	0.3
-7	1.4	-1.7
-6	14.3	-13.2
-5	0.0	0.4
-4	7.2	5.8
-3	8.1	8.2
-2	26.5	26.7
-1	23.5	23.3
0	7.3	-8.7
1	20.8	-25.5
2	1.3	-2.1
3	7.2	-8.2
4	6.6	-6.8
5	4.5	-4.1
6	4.7	-5.1
7	0.0	1.1
5	4	L
-8	2.1	2.2
-7	5.5	5.9
-6	12.5	-11.6
-5	6.0	-5.3
-4	7.7	-7.5
-3	1.4	-1.0
-2	6.4	6.2
-1	8.9	-10.6
0	10.2	11.8
1	10.0	-10.1
2	5.3	-5.9
3	5.5	-6.9
4	6.0	6.3
5	7.3	-8.4
6	5.9	4.8
5	5	L
-8	3.2	3.8
-7	4.6	5.0
-6	0.0	-2.0
-5	3.9	-4.3
-4	10.5	-8.8
-3	9.5	-8.7
-2	9.2	-9.8
-1	8.6	9.4
0	4.9	-4.7
1	17.0	19.0
2	13.6	14.3
3	2.6	2.8
4	0.0	1.4
5	3.4	-3.3
6	0.0	-0.2
5	6	L
-6	0.0	1.1
-5	4.0	3.4
-4	0.0	-1.7
-3	14.2	14.4
-2	20.1	-24.0
-1	9.1	8.5
0	5.6	5.3
1	1.5	2.1
2	0.0	1.1
3	10.0	11.3
4	5.1	-4.8
5	5.7	-5.0
5	7	L
-6	3.9	3.5
-5	0.0	1.1
-4	3.6	3.6
-3	6.4	6.0
-2	4.6	5.3
-1	22.7	-24.5
0	1.5	-1.7
1	2.0	2.6
2	9.5	-11.0
3	0.0	0.6
4	3.0	3.0
5	8	L
-6	5.5	6.5
-5	4.6	-3.8
-4	9.2	8.7
-3	8.8	-9.9
-2	7.9	9.2
-1	4.6	-4.6
0	9.0	-9.4
1	0.0	1.3
2	3.5	2.5
5	9	L
-3	4.3	4.5
-2	1.7	-1.8
-1	3.3	2.9
0	7.1	6.2
6	-9	L
0	3.4	4.1
1	9.4	-8.8
2	4.5	-4.7
6	-8	L
0	19.0	15.7
1	18.6	-18.1
2	7.8	6.7
3	2.3	-2.8
4	6.1	5.1
5	4.1	-4.6
6	-7	L
0	11.7	11.3
1	7.7	-8.7
2	0.0	1.6
3	10.7	10.6
4	0.0	-0.9
5	7.9	7.5
6	8.1	-9.5
6	-6	L
-2	2.5	-3.1
-1	10.3	11.8
0	12.0	-12.9
1	6.4	6.4
2	12.9	-12.6
3	5.1	5.8
4	10.6	10.0
5	4.2	-3.8
6	6.0	5.8
7	17.9	-23.1
6	-5	L
-3	8.9	-10.8
-2	0.0	-1.4
-1	20.4	23.8
0	16.0	-16.7
1	4.4	-3.1
2	2.6	-1.9
3	12.5	-13.3
4	18.4	19.7
5	11.4	12.7
6	12.3	-12.3
7	8.9	9.6
6	-4	L
-4	0.0	1.6
-3	0.0	-3.6
-2	10.6	8.6
-1	0.0	1.5
0	0.0	0.3
1	5.3	-5.8
2	3.5	-3.3
3	3.6	-2.9
4	2.6	-5.0
5	32.1	34.7
6	17.5	-19.6
7	5.2	5.1
6	-3	L
-5	10.5	12.8
-4	0.0	-1.4
-3	21.5	-22.1
-2	29.8	29.1
-1	10.1	-9.5
0	10.9	-9.1
1	1.5	0.9
2	6.8	-4.7
3	0.0	0.6
4	1.8	-1.6
5	4.5	-4.8
6	2.5	2.7
7	3.6	-3.4
6	-2	L
-6	5.9	-7.1
-5	8.9	-11.1
-4	11.0	11.6
-3	8.4	-7.7
-2	8.3	6.8
-1	10.3	8.7
0	1.3	1.9
1	9.4	-9.7
2	0.0	-0.5
3	15.6	-13.5
4	23.1	22.1
5	19.4	-19.3
6	1.8	0.6
7	5.3	5.2
6	-1	L
-6	6.2	7.6
-5	5.5	-5.7
-4	25.8	-26.3
-3	42.6	41.0
-2	7.2	3.6
-1	2.0	1.1
0	8.0	9.2
1	3.5	-2.3
2	7.3	-5.3
3	0.0	-1.1
4	4.3	4.7
5	1.8	-2.1
6	5.0	4.2
7	0.0	2.6
8	4.8	-5.6
6	0	L
-8	4.2	3.9
-7	5.8	6.5
-6	2.7	-2.6
-5	13.5	13.4
-4	32.3	-29.6
-3	5.7	5.2
-2	11.8	10.6
-1	4.2	-1.8
0	9.2	9.3
1	2.5	1.8
2	13.1	-10.8
3	19.3	17.6
4	6.3	-5.8
5	12.3	-12.9
6	2.2	2.1
7	0.0	1.4
8	5.7	-5.2
6	1	L
-6	8.9	12.9
-5	19.8	-23.0
-4	0.0	-1.7
-3	19.1	-15.1
-2	9.7	-6.6
-1	14.6	-13.2
0	12.8	11.1
1	12.6	11.3
2	6.1	-5.5
3	17.2	15.8
4	0.0	-0.8
5	7.4	-9.3
6	3.0	-2.1
7	0.0	-2.8
8	2.8	3.1
6	2	L
-6	16.8	22.5
-5	0.0	-2.0
-4	1.7	-3.2
-3	6.3	4.8
-2	11.0	-7.9
-1	4.1	3.6
0	16.2	-14.2
1	9.8	9.0
2	8.3	7.2
3	9.1	9.4
4	4.5	4.5
5	2.6	1.4
6	0.0	-0.5
7	0.0	-1.7
6	3	L
-5	17.7	23.2
-4	9.5	11.0
-3	6.7	6.3
-2	13.9	-11.8
-1	6.7	6.0
0	8.9	-8.2
1	29.0	-26.6
2	9.8	9.4
3	0.0	0.7
4	1.8	0.8
5	10.8	11.4
6	3.7	-2.8
7	5.1	-5.4
6	4	L
-5	0.0	-3.2
-4	15.1	17.0
-3	12.5	-12.9
-2	0.0	0.2
-1	8.9	-8.3
0	9.2	8.4
1	17.3	-16.7
2	9.9	-9.6
3	3.2	2.5
4	2.5	-4.7
5	8.4	8.9
6	4.5	4.7
6	5	L
-5	7.1	-9.6
-4	10.4	12.1
-3	8.2	-8.9
-2	0.0	-0.6
-1	17.9	17.2
0	5.4	5.0
1	10.1	9.9
2	7.4	-6.4
3	11.7	-11.1
4	0.0	1.3
5	3.0	2.8
6	6	L
-5	5.7	7.9
-4	1.8	2.8
-3	6.8	7.0
-2	10.7	-11.8
-1	7.8	9.3
0	12.5	13.0
1	0.0	-1.3
2	5.0	6.7
3	12.0	-12.9
4	4.6	-4.3
6	7	L
-1	11.3	-13.6
0	7.7	8.4
1	3.7	4.4
2	6.5	-4.8
6	8	L
0	5.5	-6.0
1	16.1	16.8
7	0	L
-7	2.5	-3.3
-6	13.2	-13.9
-5	0.0	2.3
-4	0.0	-2.0
-3	19.1	17.3
-2	21.0	19.1
-1	15.6	-13.2
0	0.0	-0.3
1	10.7	7.6
2	19.4	18.0
3	32.5	-28.9
4	10.7	10.0
5	5.9	-4.6
6	5.6	5.4
7	0.0	0.3
8	0	L
-6	3.5	2.9
-5	4.5	-3.6
-4	7.1	5.6
-3	14.4	12.3
-2	14.6	13.4
-1	28.3	-27.1
0	0.0	3.8
1	4.8	5.1
2	8.7	-9.7
3	25.4	22.8
4	5.0	-3.4
5	0.0	-2.1
6	8.3	6.8
9	0	L
-6	0.0	-0.3
-5	5.4	6.0
-4	0.0	-4.0
-3	0.0	-0.8
-2	0.0	0.4
-1	20.7	-18.2
0	16.5	14.0
1	10.6	9.8
2	0.0	-0.2
3	3.0	2.7
4	7.5	6.1
5	0.0	0.1
6	7.8	-7.0
10	0	L
-5	8.9	6.3
-4	6.2	-5.2
-3	0.0	0.9
-2	5.0	-4.7
-1	4.2	-3.5
0	9.9	8.7
1	6.3	4.9
2	3.5	-3.3
4	9.0	-6.0
5	5.2	-5.2
11	0	L
-4	5.1	3.0
-3	4.3	-3.4
-2	0.0	3.1
-1	11.7	-9.2
0	5.6	4.6
1	0.0	-0.0
2	6.0	-4.2

Coordinates and thermal factors were refined in a full-matrix least-squares procedure minimizing the function $\Sigma w(F_o-F_c)^2$ were $w=0.5$ for $F_o=0$, $w=1$ for $0<|F_o|<15$, and $w=15/|F_o|$ for $|F_o|>15$. The atomic scattering factors used were those listed in *International Tables for X-ray Crystallography* (1962). At $R=11.3\%$, a difference map was computed from which the positions of the 14 hydrogen atoms were found (Fig. 1). Inclusion of the hydrogen atoms with constant parameters and $B=2.0-2.5$ Å^2 in subsequent cycles of least-

Table 5. *Fractional coordinates* for the thymine-thymine adduct*

The thermal parameters are of the form

$T = \exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)\right]$ ($\times 10^4$).

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	0·9025	0·3886	0·6578	36	54	73	0	11	38
C(2)	1·0150	0·2986	0·6256	37	69	81	8	−6	31
N(3)	1·0220	0·1486	0·6885	43	69	118	14	24	52
C(4)	0·9146	0·0907	0·7849	75	55	61	−1	−6	25
C(5)	0·8094	0·2165	0·8659	53	57	39	−10	−10	24
C(6)	0·7718	0·3355	0·7319	58	43	46	1	−5	17
C(7)	0·8731	0·3101	1·0395	87	89	47	−6	−24	8
O(8)	1·1182	0·3402	0·5435	56	107	169	3	36	86
O(9)	0·9140	−0·0503	0·8074	105	64	156	16	41	59
O(10)	0·6816	0·1371	0·8982	59	77	41	−16	2	35
N(11)	0·4970	0·1080	0·3303	44	106	32	12	−11	18
C(12)	0·6370	0·0780	0·3244	61	55	32	2	0	24
N(13)	0·7240	0·1523	0·4599	33	62	46	10	7	19
C(14)	0·6675	0·2579	0·5877	38	46	37	−1	5	33
C(15)	0·5249	0·2962	0·5967	56	59	51	10	10	24
C(16)	0·4401	0·2170	0·4621	51	91	66	18	9	33
C(17)	0·4597	0·4148	0·7450	78	100	90	15	16	−11
O(18)	0·6867	−0·0180	0·1968	94	83	37	14	28	3
W	0·2699	0·2842	0·0894	157	90	131	−38	40	−9
Standard deviations									
C	0·0007	0·0006	0·0006	10	7	7	6	6	6
N	0·0006	0·0005	0·0005	8	6	7	6	6	6
O	0·0005	0·0005	0·0006	7	6	7	5	5	5

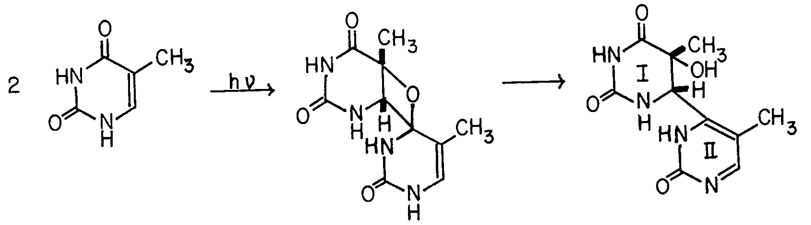
* These coordinates are related to the labeled heavy atoms in Fig. 1 by a center of symmetry.

squares refinement reduced the *R* value to 10·2%. Observed and calculated structure factors are listed in Table 4. Fractional coordinates and thermal parameters for the non-hydrogen atoms are listed in Table 5, while the approximate coordinates for the hydrogen atoms are shown in Table 6.

The configuration of the molecule is illustrated in the pair of stereodiagrams in Fig. 2 (Johnson, 1965).

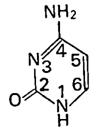
Discussion

The formation of the thymine–thymine adduct from the irradiation of thymine may proceed through an intermediate (Varghese & Wang, 1968):



The transfer of an oxygen atom from one thymine moiety to another creates a 5-hydroxydihydrothymine moiety, ring I. However, the CH_3 group on C(5) is in an axial position in contrast to dihydrothymine and dihydrothymidine where the CH_3 group is equatorial. The bond lengths and angles in this part of the molecule, illustrated in Fig. 3(*a*) and (*b*), are comparable with those found in dihydrothymine (Furberg & Jensen, 1968) and in dihydrothymidine (Konnert, Karle & Karle, to be published).

In ring II a carbonyl oxygen atom has been replaced with a single bond to C(6) of ring I in an axial position. Ring II differs from thymine in several respects: there is one less H atom on the ring and the evidence from the difference map, Fig. 1, indicates that an H atom exists on N(13), whereas the one on N(11) has been removed. (The numbering system for ring II differs from the conventional one for nucleic acids by the addition of 10 to each of the numbers.) In the cytosine molecule,



which is quite similar to ring II of the thymine–thymine adduct except for the NH_2- and CH_3-groups, the proton was found on N(1) (Barker & Marsh, 1964). To form some types of hydrogen-bonded nucleic acid pairs, a proton must exist on N(3) as found in the present investigation. Langridge & Rich (1963) interpreted an X-ray fibre diagram for one form of polycytidylic acid in terms of a molecular model which requires N(3) to be protonated. The two cases are not analogous, however, since in the present structure N(13) is not involved in hydrogen bonding and N(11) is not bonded to an extracyclic atom as is the case for polycytidylic acid.

Table 6. *Approximate coordinates for the hydrogen atoms as derived from the difference map*

	x	*y*	*z*
H(1)	0·883	0·475	0·592
H(3)	1·117	0·092	0·667
H(6)	0·733	0·417	0·792
H(7·1)	0·883	0·245	1·141
H(7·2)	0·830	0·425	1·075
H(7·3)	0·992	0·342	1·033
H(10)	0·683	0·058	0·983
H(13)	0·833	0·133	0·467
H(16)	0·333	0·222	0·462
H(17·1)	0·478	0·375	0·892
H(17·2)	0·483	0·517	0·767
H(17·3)	0·362	0·400	0·728
H(*W*1)	0·200	0·217	0·150
H(*W*2)	0·317	0·205	0·000

Bond distances and angles in ring II are compared in Table 7 with those found in thymine monohydrate (Gerdil, 1961) and cytosine (Barker & Marsh, 1964). The molecular parameters in cytosine.H_2O (Jeffrey & Kinoshita, 1963) and cytidine (Furberg, Petersen & Rømming, 1965) are very similar to those of cytosine and are not listed. Although many distances and angles are comparable, large differences (marked with an asterisk in Table 7) occur between ring II and thymine in the vicinity of C(14) where the carbonyl group has been replaced by a single bond ring I. In fact, the bond lengths and angles about C(14) are closer to those found in cytosine. At C(14) cytosine has an NH_2 group with some double bond character in the C–N bond which is an intermediate case between the C=O of thymine and the single C–C bond in the thymine–thymine adduct. Therefore, it would be expected that both ring bonds about C(14) would be shorter and the interior ring angle larger in the adduct as has been found.

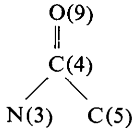
Equations for the least-squares planes are

$$1\cdot49606x+6\cdot91474y-4\cdot97139z=-0\cdot13909 \quad (1)$$

for the six ring atoms in ring II, and

$$3\cdot85396x+2\cdot67997y+5\cdot92351z=8\cdot41681 \quad (2)$$

for atoms N(1), C(2), N(3) and C(4) of ring I. The quantity on the right is the plane-to-origin distance in Å units and the *x*,*y*,*z* quantities refer to the coordinates in the triclinic cell. Fig. 4 illustrates the deviations of atoms from these least-squares planes. Ring II is very slightly buckled with the carbonyl oxygen atom 0·06 Å out of the plane of the ring; however, the carbonyl group itself with the two adjacent N atoms is coplanar to within 0·003 Å. In the dihydrothymine moiety, the ring is in the half-chair conformation with C(5) 0·412 Å above and C(6) 0·208 Å below the plane of the other four atoms. The



group forms a plane with the largest deviation being 0·020 Å and this group twists 16° about the N(3)–C(4)

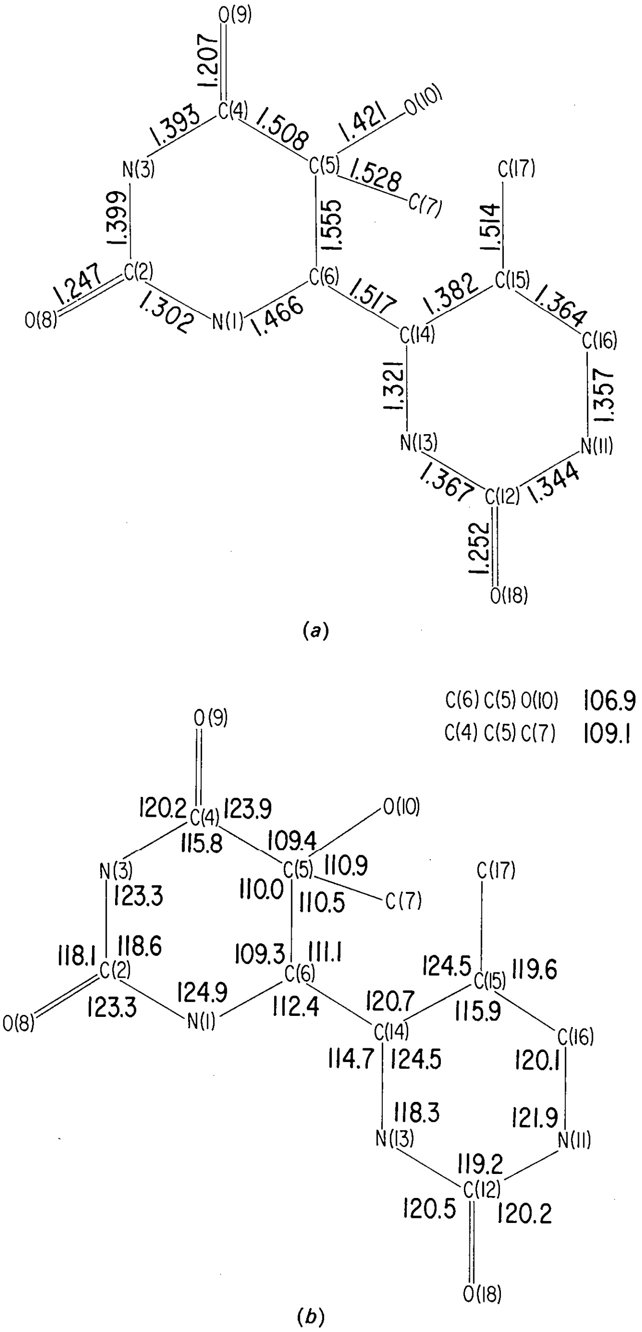


Fig. 3. (*a*) Bond lengths in Å units. The standard deviations based solely on the least-squares fit are 0·009 Å. (*b*) Angles in degrees. The standard deviations are ~0·5°.

bond from the plane of N(1), C(2), N(3), C(4). Hence O(9) must necessarily be a considerable distance from the plane of equation (2).

The packing of the molecules is dominated by a three-dimensional network of hydrogen bonds, Fig. 5. A dimer is formed around the crystallographic center at $0,\frac{1}{2},\frac{1}{2}$ by the pair of hydrogen bonds N(1)...O(8′) and N(1′)···O(8). The *x* coordinates for the unprimed atoms are 1·0 less than the coordinates shown in Table 5, except for *W*.) This dimer is similar to one formed in the thymine monohydrate crystals. The N(3)···O(18′) distance is fairly large, 3·10 Å; however, N(3), H(3) and O(18′) are all in a proper orientation for the formation of hydrogen bond. The carboxyl oxygen atom O(18) is also hydrogen-bonded to the hydroxyl group oxygen atom O(10) and the water molecule *W*. The other proton on the water molecule is directed toward O(9) of the second carbonyl group of ring I. Thus the hydrogen-bonding forms infinite chains of molecules along the *bc* diagonal and the chains are connected in the **c** direction by the O(10)H···O(18″) bonds.

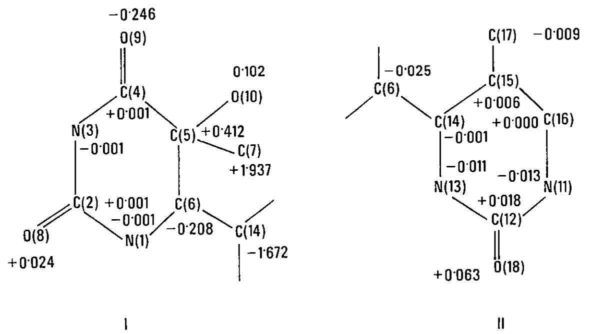


Fig. 4. Deviations in Å units from the least-squares planes computed for atoms N(1), C(2), N(3) and C(4) in ring I and the six ring atoms in ring II.

There is one other close intermolecular approach in this crystal and that is N(11)...O(10) at 2·96 Å. For a hydrogen bond to be formed between these two atoms a proton is needed at N(11) since the proton on O(10) is directed toward O(18). The difference map indicated no electron density near N(11); rather, density was found near N(13) at a suitable place for a hydrogen atom. In addition, the orientation of the covalent bonds about N(11) is unfavorable with respect to hydrogen bond formation between N(11) and O(10) since, if an H atom is assumed on N(11) lying in the plane of the ring, then the N(11)H...O(10) angle is less than 150°. The sum of the van der Waals radii for O...N contacts is 2·9 Å, comparable with the N(11)...O(10) separation.

Methyl groups occupy the spaces in the crystal which are devoid of hydrogen bonding. The region near $y=\frac{1}{2}$, $z=0$ is filled with three H atoms each from C(7), C(17) and their centrosymmetric equivalents.

The author wishes to thank Dr Sydney Wang of the Johns Hopkins University for furnishing the crystal and for helpful information and Dr Bernhard Witkop of the National Institutes of Health for his continuing interest.

Table 8. *Hydrogen bond lengths and nearest intermolecular approach*

Bond	Length
N(1)H····O(8′)	2·91 Å
N(3′)H···O(18)	3·10
O(10)H···O(18)	2·77
*W*H·····O(18′)	2·88
*W*H·····O(9′)	2·82
N(11′)····O(10)	2·96

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Table 7. *Comparison of bond distances and angles*†

Bond length	Thymine–thymine adduct. H_2O (ring II)	Cytosine	Thymine. H_2O
N(11)–C(12)	1·344	1·374	1·355
C(12)–O(18)	1·252	1·234	1·234
C(12)–N(13)	1·367	1·364	1·361
*N(13)–C(14)	1·321	1·337	1·391
*C(14)–C(15)	1·382	1·424	1·447
C(15)–C(17)	1·514		1·503
C(15)–C(16)	1·364	1·342	1·349
C(16)–N(11)	1·357	1·357	1·382
Bond angle			
N(11)C(12)N(13)	119·2°	118·1°	115·2°
*C(12)N(13)C(14)	118·3	119·9	126·3
*N(13)C(14)C(15)	124·5	122·0	115·6
C(14)C(15)C(16)	115·9	117·3	118·2
C(15)C(16)N(11)	120·1	120·1	121·8
C(16)N(11)C(12)	121·9	122·7	122·8

† The e.s.d. for the bond lengths are 0·002 Å for thymine. H_2O, 0·003 Å for cytosine and 0·009 Å for the adduct. The largest e.s.d. for the angles is 0·5°.

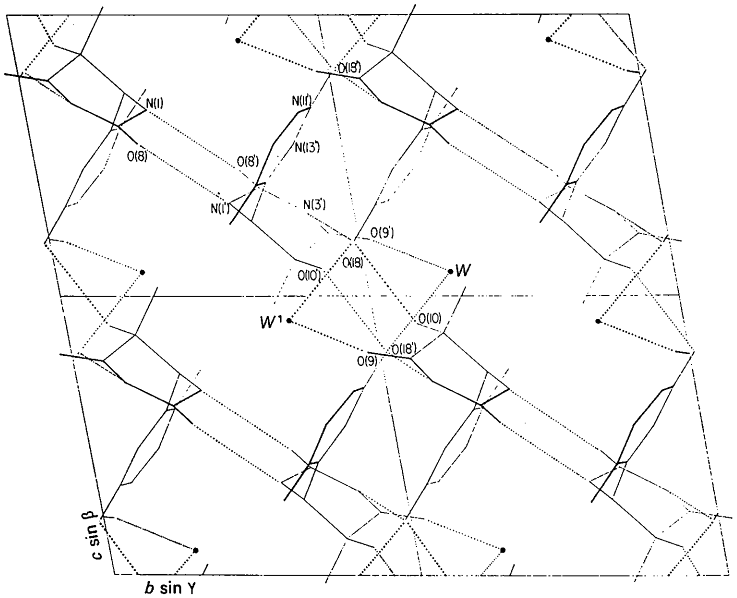

Fig. 5. Contents of four unit-cells illustrating the hydrogen bonding and molecular packing.

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