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The Crystal and Molecular Structure of the *cis-syn* Photodimer of Uracil

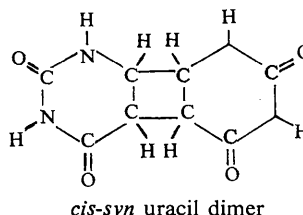
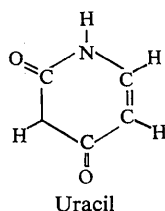
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The *cis-syn* photodimer ($C_8H_8N_4O_4$) of uracil, formed upon ultraviolet irradiation of the monomer in frozen aqueous solution, crystallizes in the monoclinic system with cell dimensions $a = 13.249 \pm 0.001$, $b = 11.191 \pm 0.001$, $c = 6.279 \pm 0.0003$ Å, $\beta = 94.751 \pm 0.004^\circ$, space group $P2_1/n$. The molecules exhibit a non-planar cyclobutane ring and non-planar heterocyclic rings, with bond lengths and angles characteristic of each portion. All possible hydrogen bonds are formed, holding the molecules together in an extensive three-dimensional network.

Irradiation of pyrimidines and their derivatives with ultraviolet light under various conditions produces dimers with a cyclobutane linkage formed by joining the monomers at the 5-6 double bond, *i.e.*



Uracil, thymine, and mixed uracil-thymine dimers have been isolated from irradiated deoxyribonucleic acid

(DNA) *in vitro* (Setlow & Carrier, 1966) and, along with other photoproducts, are involved in the loss of activity of DNA. Uracil dimers have also been isolated from TMV-RNA (tobacco mosaic virus ribonucleic

acid), but their role is less well defined (Merriam & Gordon, 1967).

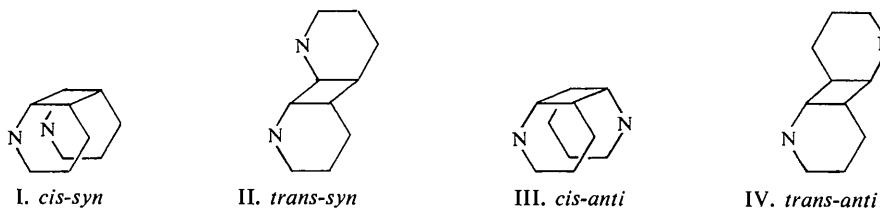
Table 1. *Examples of pyrimidine photodimers with known structures*

Isomer	Monomer	Source	Method of identification*	References
I <i>cis-syn</i>	Uracil	Frozen aqueous solution	Chemical degrad. XRD	Dönges & Fahr (1966) This work
	Thymine	Frozen aqueous solution	Chemical degrad. XRD	Blackburn & Davies (1967) Kuneida & Witkop (1967) Wei & Einstein (1968)
III <i>cis-anti</i>	Dimethylthymine	<i>E. coli</i> DNA	Chemical degrad.	Blackburn & Davies (1967)
	Dimethylthymine	Frozen aqueous solution	XRD	Camerman & Camerman (1968)
IV <i>trans-anti</i>	Thymine	Frozen aqueous solution of thymidine	XRD	Camerman, Weinblum & Nyburg (1969)
	1-methylthymine	Frozen aqueous solution	XRD	Camerman & Nyburg (1969)
				Einstein, Hosszu, Longworth, Rahn & Wei (1967)

* XRD, X-ray diffraction.

Beukers & Berends (1961) reported the formation of a dimer of thymine in frozen aqueous solution of monomer and adduced some evidence for the cyclobutane nature of the linkage. Also, Wang (1961) and Smietanowska & Shugar (1961) reported isolation of a uracil dimer from the same medium, thus initiating a large number of investigations into the dimeric structures.

The four possible isomers of pyrimidine dimers originally pointed out by Wulff & Fraenkel (1961) are:



Examples of three of the four types have been unequivocally identified by chemical degradation or X-ray diffraction methods, and are listed in Table 1. These

identifications confirm the initial assignments of the structures made by several earlier workers (Stewart, 1963; Wang, 1963; Anet, 1965; Weinblum & Johns, 1966; Blackburn & Davies, 1966; Hollis & Wang, 1967; Varghese & Wang, 1967; Morrison, Feeley & Kloefer, 1968). Thus, comparison of chromatographic, nuclear magnetic resonance and spectral properties with those of the known structures has shown that the major form of the dimeric photoproduct iso-

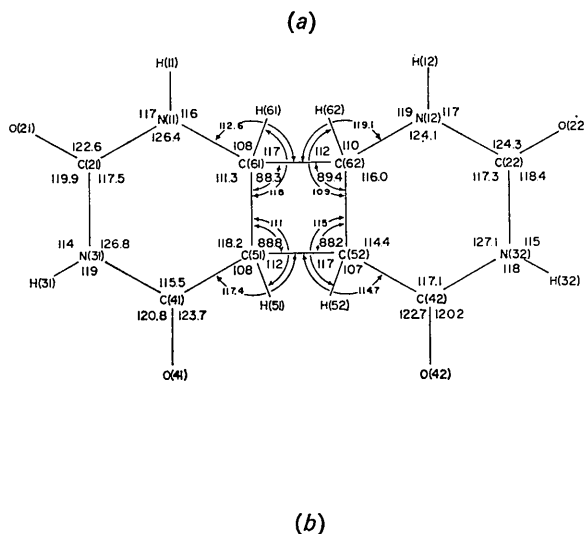
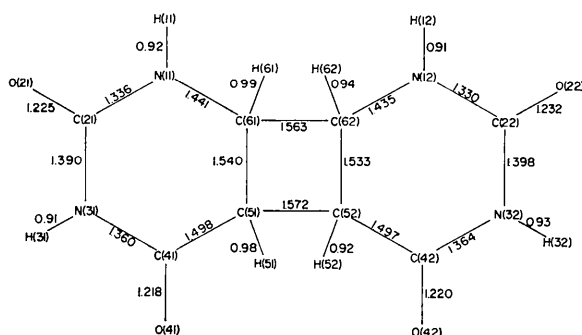


Fig. 1. *cis-syn* uracil photodimer (a) bond lengths (b) bond angles.

lated from irradiated frozen solution and from native DNA is the *cis-syn* type, although recent work has indicated that another type, the *trans-syn* (isomer II) may be formed upon irradiating denatured DNA (Ben-Hur & Ben-Ishia, 1968). The spatial arrangement of the *cis-syn* type of dimer is of particular interest in deducing what may happen to the local structure of DNA upon irradiation, and accordingly the present study was undertaken to provide accurate parameters describing the arrangement. Two recent studies on *cis-syn* thymine dimer derivatives (Camerman & Camerman, 1968; Wei & Einstein, 1968) also provide such information, although monomerization of the thymine dimers by X-ray irradiation complicates the picture somewhat.

Experimental

Preparation

Aliquots, 125 ml each, of a solution of uracil in water (0.5 mg.ml^{-1}) were frozen in Pyrex baking dishes ($9 \times 13 \text{ in}$) and irradiated in a freezer for 15 minutes using two General Electric germicidal lamps (15 W) at a distance of approximately 3 in. The irradiated solutions were thawed and stirred, refrozen and reirradiated for 15 minutes more. Preliminary work indicated that 70% conversion to dimer was achieved after these steps. The material was then treated essentially according to Ishihara (1963) and recrystallized from hot water. Tiny crystals formed initially and were used as seed to grow several crystals of a size suitable for X-ray diffraction intensity measurements.

Data collection

A chunky prismatic crystal of approximate dimensions $0.21 \times 0.21 \times 0.27 \text{ mm}$ was used for all X-ray measurements. The crystals are monoclinic and the absence of $h0l$ reflections where $h+l=2n+1$ and $0k0$ where $k=2n+1$ indicates the probable space group to be $P2_1/n$. The cell dimensions, $a = 13.249 \pm 0.001$, $b = 11.191 \pm 0.001$, $c = 6.279 \pm 0.0003 \text{ \AA}$, $\beta = 94.751 \pm$

0.004°, were determined by a least-squares refinement using measurements of both positive and negative 2θ values for 20 reflections ($\lambda_{\text{Cu } K\alpha} = 1.5418 \text{ \AA}$). The calculated density is 1.605 g.cm^{-3} for four dimers per unit cell. Intensity measurements were made with Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) for 2135 reflections using the $\omega/2\theta$ scan mode on a manual diffractometer equipped with a quarter-circle goniostat. The crystal was mounted along c^* . Background counts were measured for one-half the scan time at each limit of the scan

range. Of the 2135 reflections, 507 were observed to be less than twice the estimated error in measurement; these were set equal to 2σ and coded as unobserved.

The data were modified for Lorentz and polarization effects but were not corrected for absorption since the calculated linear absorption coefficient, μ , is 1.4 cm^{-1} , and the crystal shape was fairly regular. A correction for coincidence loss of the scintillation counter was also made. This correction amounted to a 6% increase in the intensity of the largest reflection (86,000 deka-

Table 2. Observed and final calculated structure factors ($\times 10$)

h	k	l	Observed	Final	h	k	l	Observed	Final
0	0	0	86000	86000	10	0	0	100	100
0	0	1	100	100	10	1	0	100	100
0	0	2	100	100	10	2	0	100	100
0	0	3	100	100	10	3	0	100	100
0	0	4	100	100	10	4	0	100	100
0	0	5	100	100	10	5	0	100	100
0	0	6	100	100	10	6	0	100	100
0	0	7	100	100	10	7	0	100	100
0	0	8	100	100	10	8	0	100	100
0	0	9	100	100	10	9	0	100	100
0	0	10	100	100	10	10	0	100	100
0	0	11	100	100	10	11	0	100	100
0	0	12	100	100	10	12	0	100	100
0	0	13	100	100	10	13	0	100	100
0	0	14	100	100	10	14	0	100	100
0	0	15	100	100	10	15	0	100	100
0	0	16	100	100	10	16	0	100	100
0	0	17	100	100	10	17	0	100	100
0	0	18	100	100	10	18	0	100	100
0	0	19	100	100	10	19	0	100	100
0	0	20	100	100	10	20	0	100	100
0	1	0	100	100	11	0	0	100	100
0	1	1	100	100	11	1	0	100	100
0	1	2	100	100	11	2	0	100	100
0	1	3	100	100	11	3	0	100	100
0	1	4	100	100	11	4	0	100	100
0	1	5	100	100	11	5	0	100	100
0	1	6	100	100	11	6	0	100	100
0	1	7	100	100	11	7	0	100	100
0	1	8	100	100	11	8	0	100	100
0	1	9	100	100	11	9	0	100	100
0	1	10	100	100	11	10	0	100	100
0	1	11	100	100	11	11	0	100	100
0	1	12	100	100	11	12	0	100	100
0	1	13	100	100	11	13	0	100	100
0	1	14	100	100	11	14	0	100	100
0	1	15	100	100	11	15	0	100	100
0	1	16	100	100	11	16	0	100	100
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0	1	19	100	100	11	19	0	100	100
0	1	20	100	100	11	20	0	100	100
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0	2	1	100	100	12	1	0	100	100
0	2	2	100	100	12	2	0	100	100
0	2	3	100	100	12	3	0	100	100
0	2	4	100	100	12	4	0	100	100
0	2	5	100	100	12	5	0	100	100
0	2	6	100	100	12	6	0	100	100
0	2	7	100	100	12	7	0	100	100
0	2	8	100	100	12	8	0	100	100
0	2	9	100	100	12	9	0	100	100
0	2	10	100	100	12	10	0	100	100
0	2	11	100	100	12	11	0	100	100
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0	2	13	100	100	12	13	0	100	100
0	2	14	100	100	12	14	0	100	100
0	2	15	100	100	12	15	0	100	100
0	2	16	100	100	12	16	0	100	100
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0	2	18	100	100	12	18	0	100	100
0	2	19	100	100	12	19	0	100	100
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0	3	16	100	100	13	16	0	100	100
0	3	17	100	100	13	17	0	100	100
0	3	18	100	100	13	18	0	100	100
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0	3	20	100	100	13	20	0	100	100
0	4	0	100	100	14	0	0	100	100
0	4	1	100	100	14	1	0	100	100
0	4	2	100	100	14	2	0	100	100
0	4	3	100	100	14	3	0	100	100
0	4	4	100	100	14	4	0	100	100
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0	4	6	100	100	14	6	0	100	100
0	4	7	100	100	14	7	0	100	100
0	4	8	100	100	14	8	0	100	100
0	4	9	100	100	14	9	0	100	100
0	4	10	100	100	14	10	0	100	100
0	4	11	100	100	14	11	0	100	100
0	4	12	100	100	14	12	0	100	100
0	4	13	100	100	14	13	0	100	100
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0	4	16	100	100	14	16	0	100	100
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0	5	3	100	100	15	3	0	100	100
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0	5	8	100	100	15	8	0	100	100
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0	5	10	100	100	15	10	0	100	100
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0	6	7	100	100	16	7	0	100	100
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0	6	13	100	100	16	13	0	100	100
0	6	14	100	100	16	14	0	100	100
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0	6	19	100	100	16	19	0	100	100
0	6	20	100	100	16	20	0	100	100
0	7	0	100	100	17	0	0	100	100
0	7	1	100	100	17	1	0	100	100
0	7	2	100	100	17	2	0	100	100
0	7	3	100	100	17	3	0	100	100
0	7	4	100	100	17	4	0	100	100
0	7	5	100	100	17	5	0	100	100
0	7	6	100	100	17	6	0	100	100
0	7	7	100	100	17	7	0	100	100
0	7	8	100	100	17</				

The correct set of signs is usually the one with the highest consistency index defined as

$$C = \frac{\langle E_h \sum_k E_{h-k} E_k \rangle}{\langle |E_h| \sum_k |E_{h-k}| |E_k| \rangle}$$

In this case the correct set had a consistency index of 0.81; the next highest with a different set of signs was 0.66. Three other sets of signs with consistency indices between 0.81 and 0.66 were, in fact, the same as the correct set, but arrived at by a different path. The set with consistency index = 0.81 was used in an *E* map (Karle, Hauptman, Karle & Wing, 1958) which clearly showed peaks corresponding to all non-hydrogen atomic positions.

Refinement

In the refinements of the structure the scattering factors for carbon and nitrogen were those of McWeeny (1951); for oxygen those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); for hydrogen those of *International Tables for X-ray Crystallography* (1962). The quantity minimized was $\sum_w (|F_o| - |F_c|)^2$ in which the weights *w* were set equal to $1/\sigma_F^2$. The errors in the *F* values were taken as

$$\sigma_F = \sigma_I / 2(I L_p)^{1/2} \quad (6)$$

where

$$\sigma_I = [\sigma_t + (S \cdot t)^2]^{1/2}$$

and *I* = intensity and *L_p* = Lorentz polarization correction. The error in *I* includes the error estimated from

counting statistics, σ_t , where *t* is equal to the total counts measured for the reflection (background plus peak), and the error due to machine or other instability, approximated by the product of *t* and the parameter *S*. The latter was estimated from the plot of four standards monitored every four hours throughout data collection. Initially *S* was set equal to 0.01 for the first half of the data and 0.02 for the second half, these values approximating one-half the maximum relative excursion between consecutive standards. Subsequently, however, *S* was taken as 0.02 for all the data in view of the appreciable deterioration of the crystal. It should be noted that this may bias the weights somewhat if the use of the larger value for *S* does indeed reflect the non-random effect of deterioration.

Three refinement cycles, in which the scale, positional and isotropic thermal parameters were varied, reduced *R* ($= \sum_{hkl} ||F_o| - |F_c|| / \sum_{hkl} |F_o|$) to 0.13 and *R_w*

($= \sum_{hkl} w ||F_o| - |F_c|| / \sum_{hkl} w |F_o|$) to 0.14 for the observed re-

flections only. Two additional refinement cycles with anisotropic thermal parameters reduced the conventional *R* to 0.084 and *R_w* to 0.105. The eight hydrogen atom positions were located from a ΔF synthesis and along with isotropic thermal parameters were included in two additional refinement cycles: *R* decreased to 0.056, *R_w* to 0.079.

Four reflections which appeared to be in error were removed and the scattering factors for hydrogen were changed to those of Stewart, Davidson & Simpson (1965). Three more refinement cycles reduced *R* to 0.047 and *R_w* to 0.045, the change in *R* being primar-

Table 4. Comparison of bond lengths and angles among some saturated and unsaturated pyrimidine molecules

(a) Bond lengths	N(1)-C(2)	C(2)-N(3)	N(3)-C(4)	C(4)-C(5)	C(5)-C(6)	C(6)-N(1)	Reference
Pyrimidine							
<i>cis-syn</i>	1.336 Å	1.390 Å	1.360 Å	1.498 Å	1.540 Å	1.441 Å	This work
Uracil dimer	1.330	1.398	1.364	1.497	1.533	1.435	
<i>trans-anti</i>	1.334	1.390	1.357	1.508	1.547	1.440	Camerman & Nyburg (1969)
Thymine dimer							
<i>cis-anti</i>	1.342	1.426	1.378	1.509	1.533	1.431	Camerman, Weinblum & Nyburg (1969)
Dimethylthymine dimer	1.344	1.406	1.377	1.503	1.529	1.449	
Dihydrothymine	1.326	1.383	1.358	1.54	1.52	1.46	Furberg & Jensen (1968)
Dihydrouracil	1.34	1.39	1.38	1.50	1.51	1.47	Rohrer & Sundaralingam (1968)
Uracil	1.371	1.376	1.371	1.430	1.340	1.358	Stewart & Jensen (1967)
Thymine	1.355	1.361	1.391	1.447	1.349	1.382	Gerdil (1961)
(b) Bond angles	N(1)	C(2)	N(3)	C(4)	C(5)	C(6)	
<i>cis-syn</i>	126.4°	117.5°	126.8°	115.5°	118.2°	111.3°	
Uracil dimer	124.1	117.3	127.1	117.1	114.4	116.0	
<i>trans-anti</i>	125.7	116.8	127.8	117.7	115.2	116.0	
Thymine dimer							
<i>cis-anti</i>	121.7	116.9	125.8	117.7	112.1	116.3	
Dimethylthymine dimer	121.6	117.4	126.3	117.8	112.7	115.7	
Dihydrothymine	121.6	116.6	126.3	113.6	106.7	108.8	
Dihydrouracil	121	116	127	114	113	110	
Uracil	122.7	114.0	126.7	115.5	118.9	122.3	
Thymine	122.8	115.2	126.3	115.6	118.2	121.8	

ily due to editing the reflections thought to be in error. At this point, the average shift for the parameters was 0.16σ , with a maximum of 1.09σ for the B value of one hydrogen atom. The principal result of changing the hydrogen scattering factors was a change in the thermal parameters of the hydrogen atoms from a range of $-0.7-1.8$ to $1.4-4.1$ Å. Remeasuring 30 reflections (of which only 12 turned out to be significantly in error), adjusting the weights with the parameter S set equal to 0.02 for all the data and refining for two more cycles gave an R of 0.044 and R_w of 0.046. Three additional refinement cycles reduced the average shift to 0.03σ and changed R to 0.045, but there was no further change in R_w . The R for the unobserved reflections was 0.064. The highest peaks in the final difference Fourier synthesis were $0.25 \text{ e.}\text{\AA}^{-3}$, some appearing between bonded-carbon atom positions.

Results

Table 2 is a list of F_o and final F_c values, scaled by a factor of 10. The final positional and thermal parameters are listed in Table 3. Maximum values of the estimated standard deviations in C-C, C-N and C-O bond lengths are 0.0025 Å, in C-H bond lengths, 0.025 Å, in bond angles involving non-hydrogen atoms, 0.2° , and in those involving hydrogen atoms, 1.5° . Comparison of chemically identical bond lengths in the two halves of the molecule indicates that the standard deviations estimated from the inverse matrix of the least-squares refinement are reasonable. Bond lengths

and angles uncorrected for the effects of thermal motion are given in Fig. 1. A calculation using a riding model shows an upper limit of change in ring bond lengths of 0.007 Å and in C-O bond lengths, $0.01-0.02$ Å, values which are significant in view of the e.s.d.'s quoted above. Fig. 2 is a stereo plot of the molecule with thermal ellipsoids drawn at the 50% probability level. Fig. 3 illustrates the arrangement of the molecules in the unit cell.

Discussion

The molecular structure

The bond lengths and angles in the heterocyclic parts of the molecule are quite comparable with those of the other saturated pyrimidines as shown in Table 4. The close agreement between corresponding bond lengths in two different isomers of the dimer, the *trans-anti* and this one, show that although the cyclobutane conformations in each of these are different (one being planar and the other puckered and not distorted from normal cyclobutane conformations), they have little effect on the heterocyclic part. There is still considerable double-bond character in the C-N bonds, similar to that in other C-N bonds conjugated with C=O bonds as in diketopiperazine (Degeilh & Marsh, 1959) and peptides (Pauling & Corey, 1951). Since the hydrogen atoms are definitely localized on the nitrogen atoms, the molecule is in the keto form.

The bonds in the cyclobutane ring are of two kinds, inter- and intrapyrimidine ring, and as such have sig-

Table 5. Bond angles of substituents on the cyclobutane ring

'Axial'		'Equatorial'			
C(42)-C(52)-C(51)	114.7°	H(52)-C(52)-C(51)	117°		
C(42)-C(52)-C(62)	114.4	H(52)-C(52)-C(62)	115	C(42)-C(52)-H(52)	107°
N(11)-C(61)-C(62)	112.6	H(61)-C(61)-C(62)	117		
N(11)-C(61)-C(51)	111.3	H(61)-C(61)-C(51)	118	N(11)-C(61)-H(61)	108
H(62)-C(62)-C(61)	112	N(12)-C(62)-C(61)	119.1		
H(62)-C(62)-C(52)	109	N(12)-C(62)-C(52)	116.0	N(12)-C(62)-H(62)	110
H(51)-C(51)-C(52)	112	C(41)-C(51)-C(52)	117.4		
H(51)-C(51)-C(61)	111	C(41)-C(51)-C(61)	118.2	C(41)-C(51)-H(51)	108

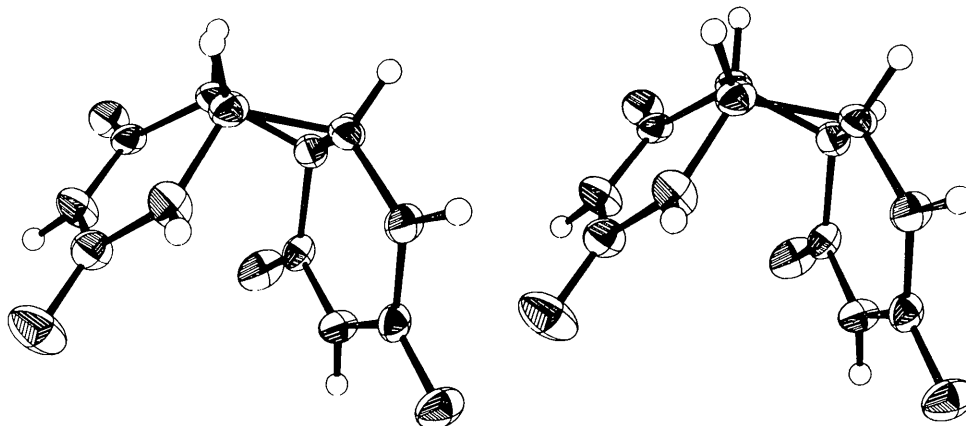


Fig. 2. Stereoscopic plot of thermal ellipsoids of *cis-syn* uracil photodimer at 50% probability level, viewed along c^* .

nificantly different bond lengths [see Fig. 1(a)]. Bond lengths in the range 1.53–1.57 Å have been reported in simply substituted cyclobutane molecules, *i.e.* where substituents are not involved in other rings as in this case (see Adman & Margulis, 1968 and references therein). In the present molecule, the interpyrimidine bond lengths are 1.572 and 1.563 Å, and although the difference between them is small, it is significant at the 1% level. The difference may well be real since one of



the bonds is between a pair of O=C-CH- groups, the



other between a pair of N-CH- groups. The interpyrimidine bond lengths observed in the *cis-anti* dimethylthymine dimer (Camerman, Weinblum & Nyburg, 1969) are not significantly different and the average value is 1.574 ± 0.003 Å. In that case, however, both



bonds are between an O=C-CH- group and an N-CH- group and should be the same length. The cyclobutane rings in both dimers are puckered and the interpyrimidine bond lengths are on the high side of the range quoted above although the longer bond lengths are usually found in planar cyclobutane molecules.

The intrapyrimidine bonds in common with the cyclobutane ring in the *cis-syn* uracil dimer are longer than the corresponding bonds in the dihydropyrimidines, and the angles at the N(1) nitrogen atoms are larger in the unmethylated dimers than the corresponding angles in the dihydropyrimidines (see Table 4). The latter effect probably results from the former which in turn stems from the fact that the C(5)-C(6) bonds are part of the cyclobutane ring.

Each pyrimidine ring is in a half-chair conformation represented schematically in Fig. 4 in terms of distance

of the atoms from a least-squares plane through the six atoms of the ring and also by the values of the torsion angles around each bond in the ring. The rings are more nearly planar than other pyrimidine rings with saturated C(5)-C(6) bonds (except for the rings in the *trans-anti* dimer): least-squares planes fit, within 0.03 Å, atoms N(1)-C(2)-N(3)-C(4)-C(5), with C(6) deviating by -0.28 and -0.26 Å from the respective planes in each ring. Individual portions of the molecule are more nearly planar than others: in both rings least-squares planes fit within 0.008 Å atoms N(1)-C(2)-O(2)-N(3); within 0.010, N(3)-C(4)-O(4)-C(5), and to within 0.015 Å, N(1)-C(2)-N(3)-C(4). The angle between the 'best' planes of the six atoms in each ring is 140°.

The cyclobutane ring is puckered, having an average dihedral angle equal to 155°, a value indicating a flatter ring than most non-planar cyclobutanes, where the range of values is 149–155°. The torsion angles within the cyclobutane rings are +17, -17, +17 and -17°. As a result of the puckering, the heterocyclic rings are twisted. A measure of the 'twist' of the rings relative to each other, *i.e.* degree of nonsuperposition when viewed along either interpyrimidine cyclobutane bond, is the average of the dihedral angles between the planes determined by C(41)-C(51)-C(52) and C(51)-C(52)-C(42) and between the planes determined by N(11)-C(61)-C(62) and C(61)-C(62)-N(12). The average is 24°, the former being 23°, the latter, 25°.

It is interesting to note that the *cis-anti* thymine dimer, which has no hydrogen bonds since the nitrogen atoms are methylated, has a slightly more puckered cyclobutane ring (dihedral angles average 153.5°) and a twist of 29°, and that the *cis-syn* dimethylthymine dimer has a twist of 28°. Either the hydrogen bonding or the lack of a methyl group on C(6) tends to open up the *cis-syn* uracil dimer in the crystal.

An additional feature, related to the puckering, is the 'axial' or 'equatorial' character of the substituents,

Table 6. Hydrogen-bond geometry

Type	Atoms in bond	O-N	O-H	C-O-N	O-H-N
I	N(32)-H(32)-O(41)	2.846 Å	1.93 Å	132.5°	172°
II	N(12)-H(12)-O(22)	2.888	1.98	120.8	177
III	N(11)-H(11)-O(42)	2.887	2.00	149.1	164
IV	N(31)-H(31)-O(21)	2.860	1.96	126.6	171

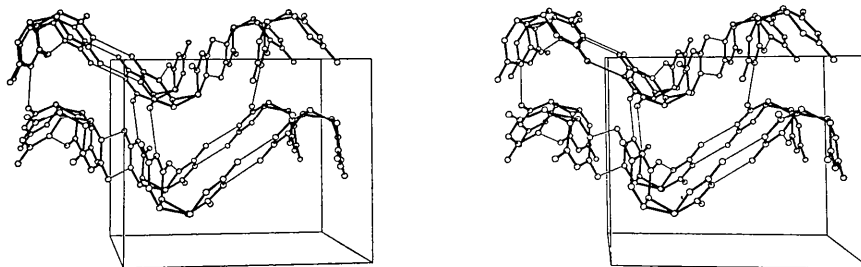


Fig. 3. Stereoscopic drawing of packing and hydrogen bonding in crystal of *cis-syn* uracil photodimer, viewed along $-c^*$. The a axis runs left to right; b , top to bottom. The origin of the unit cell is at the top, left front corner.

analogous to cyclohexane. The average value of the angle ('*A*') between the axial substituents and the mean plane of the cyclobutane ring is 20° while that ('*E*') of the equatorial substituents is 127°. The close approach [3.24 Å for N(11)–C(42)] of the transannular axial substituents forced by the small ring system determines the observed values of '*A*'; in the less crowded cyclohexane the analogous angles '*A*' and '*E*' would be 0 and 109.5° respectively. Crowding of substituents on a puckered four-membered ring also constrains the values of the angle ('*S*') between substituent bonds and ring bonds. Table 5 shows that the value of '*S*' is smaller than 115° for axial substituents and greater than 115° for equatorial substituents, whereas they should approach the normal tetrahedral value of 109.5° if they were in a less crowded ring system.

The crystal structure

The molecules are held in the crystal lattice by an extensive network of N–H...O hydrogen bonds in which all those possible are formed. The arrangement is shown in Fig. 3. Ribbons of hydrogen-bonded molecules undulate roughly parallel to [101] so that in a ribbon *ABAB*..., *A* is joined to *B* by one pair of hydrogen bonds of type I across a center of symmetry at $(\frac{1}{2} 0 1)$ and translationally equivalent positions, and *B* is joined to *A* by a second pair of hydrogen bonds, type II, across a center of symmetry at $(0 0 \frac{1}{2})$ and translationally equivalent positions. The *A* molecules are in the extreme upper left of Fig. 3, *B* at the upper left of the unit cell. The *ABAB*... ribbon corresponds to the top ribbon in Fig. 3 with type II bonds to the left and type I at the center. A second ribbon, *A'B'A'B'*..., in which *A'* is related to *A* by a screw axis, runs in the same way, except that II' is centered at $(\frac{1}{2} \frac{1}{2} 1)$ and I' at $(0 \frac{1}{2} \frac{1}{2})$. The ribbon *ABAB* is hydrogen bonded to another *ABAB* ribbon by single hydrogen bonds of type III (and III' for *A'B'A'B'*) connecting translationally equivalent molecules in the *z* direction. The sheets of *ABAB*... and *A'B'A'B'*... thus formed are then hydrogen bonded to each other by type IV single hydrogen-bonds connecting screw related molecules, thus completing the three-dimensional network. The geometry of each of these types of hydrogen bond is described in Table 6. Type III appears to be the most

distorted, another example of the variability in hydrogen-bond geometry. There are a few short intermolecular contacts, primarily between ring 2 of a *B* molecule and ring 2 of the *A* molecule related by a center of symmetry at $(\frac{1}{2} 0 \frac{1}{2})$. These are: C(22)–C(42'), 3.391 Å; C(22)–N(32'), 3.240 Å; O(22)–C(42'), 3.155 Å; C(52)–O(22'), 3.303 Å. Short distances between molecules related by the screw axis at $(\frac{1}{2} y \frac{1}{2})$ are between C(62)–O(21'), 3.303 Å; and C(41)–O(22'), 3.301 Å. An additional close approach of 3.295 Å is between C(62) and O(41) of glide-related molecules. All of these approaches can be seen to be a result of the requirements of the elaborate hydrogen bonding network.

Conclusions

The *cis-syn* uracil dimer geometry typifies two features which may be expected in the pyrimidine dimers occurring in DNA: one feature is a puckered cyclobutane ring with geometry very much like simply-substituted cyclobutane rings; the other, pyrimidine rings with characteristic changes in bond lengths in addition to those expected for the bond also contained by the cyclobutane ring. The hydrogen bonding ability of the monomer is not changed in the dimer, although in DNA the fairly strict geometric requirements for hydrogen bonding may no longer be satisfied since the relative orientation of the halves of the dimer would destroy the coplanarity of hydrogen-bonded base pairs. Just how much the DNA backbone must be distorted to accommodate this new geometry remains to be seen from studies of higher order dimers such as uridine dimer or a dimer of uridylyl-(3'-5')-uridine with the ribose-phosphate-ribose unit intact.

All computing, except where otherwise noted, was done using the programs in *X-ray-63* (Stewart, 1964). Stereo drawings were done using Johnson's (1965) *ORTEP* plotting program.

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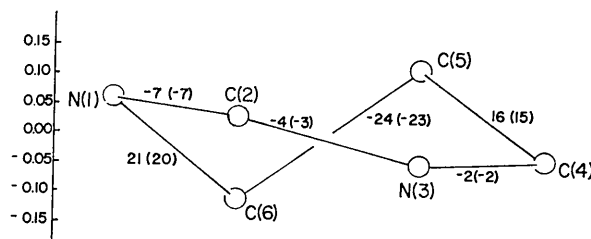


Fig. 4. A schematic plot of the distances of atoms in the heterocyclic ring from the best least-squares plane of all six. The torsion angle (in degrees, that of ring 2 in parentheses) is the angle between the normals to two least-squares planes of three ring atoms, each having a bond common to both. The sense is such that when viewing along a bond the three-atom-plane containing the bond furthest from the viewer must be rotated in a clockwise direction to eclipse the three-atom plane containing the forward-most bond.

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The Crystal Structure of Trimethylammonium Iodide; Refinement of Absorption for a Lamellar Crystal

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The crystal structure of Me_3NHI has been determined by single-crystal X-ray diffraction. The crystals are monoclinic, $P2_1/m$, $a = 7.13$, $b = 8.33$, $c = 5.62$ Å, $\beta = 104^\circ 48'$, $Z = 2$. Intensities were estimated visually from equi-inclination Weissenberg photographs; the structure was refined by full-matrix least squares to a final conventional R index of 0.147 for 431 non-zero unique reflexions. The compound is isostructural with Me_3NHBr but not with Me_3NHCl . The N-C bond lengths are 1.45 ± 0.06 and 1.46 ± 0.04 Å, and the C-N-C angles 113 ± 2 and $109 \pm 2^\circ$. There is a short, probably linear, N-H...I hydrogen bond, with an N...I distance of 3.46 ± 0.04 Å. A useful procedure for refining the linear absorption coefficient for a lamellar crystal is described.

Introduction

A complete set of X-ray data for a crystal of trimethylammonium iodide was obtained in the course of our

investigation of trimethylamine adducts of silyl halides. We have completed the structure determination because there is some interest in the N-H...I hydrogen bond length, and because it provided an opportunity