important role if the cancer-producing property of methylcholanthrene depended on intercalation with nucleic acid.

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6-Azathymine

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Abstract. $C_4H_5N_3O_2$, orthorhombic, *Pnam*, $a=6{\cdot}7313$ (7), $b=13{\cdot}0361$ (12), $c=6{\cdot}3309$ (10) Å, $Z=4$, $D_c=1{\cdot}513$, $D_m=1{\cdot}50$ (2) g cm^{-3}, $U=555{\cdot}5$ Å^3. The azapyrimidine ring is planar, and the molecular geometry is similar to that of 6-azauracil. The hydrogen-bonding scheme is different, however, involving N(1)–H(1)···O(4) and N(3)–H(3)···O(2) interactions of length 2·79 Å which give rise to a sheet-like structure perpendicular to the crystallographic *c* axis.

Introduction. Plate-like crystals of 6-azathymine were grown from aqueous solution, and the sample used had dimensions $0{\cdot}71\times0{\cdot}64\times0{\cdot}13$ mm. The data showed systematic absences of $k+l=2n+1$ for $0kl$ and $h=2n+1$ for $h0l$. The intensity data were collected using Mo $K\alpha$ radiation on a four-circle Picker automatic diffractometer with a scintillation counter and a pulse height analyzer. The incident beam was filtered through a 3·0 mil niobium foil. The cell constants were determined by the least-squares procedure of Busing & Levy (1967) using data obtained with Cu $K\alpha$ radiation filtered through 0·5 mil nickel foil. The data were corrected for Lorentz and polarization effects and for background, but not for absorption. 1113 reflections [$513>3\sigma(I)$] were measured.

Solution of the structure by direct methods (Hauptman & Karle, 1953) proved to be difficult, and so the structure was solved by means of a three-dimensional Patterson function. All hydrogen atoms were located unambiguously in a difference Fourier synthesis, and least-squares refinements were carried out in which the hydrogen atoms were refined isotropically and all other atoms were refined anisotropically. The function minimized was $\sum w(|F_o|-|F_c|)^2$, and the weights w were taken as $4F_o^2/\sigma^2(F_o)^2$. Examination of the data at a late stage of refinement suggested to us that no correction for secondary extinction was necessary.

The final agreement indices, $R_1=\sum||F_o-F_c||/\sum|F_o|$ and $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ were 0·062 and 0·083, respectively, based on 513 observations and 68 variables. Refinement in the non-centrosymmetric space group $Pna2_1$ led to a model which did not differ significantly from the centrosymmetric model and which yielded values of 0·059 and 0·076 for R_1 and R_2,

Table 1. *Positional and thermal parameters for* 6-*azathymine*

All parameters (except hydrogen isotropic thermal parameters) have been multiplied by 10^4. All anisotropically refined atoms are constrained to lie on a mirror plane in *Pnam*, so for all atoms $\beta_{13}=\beta_{23}=0{\cdot}0$ and $z=\frac{1}{4}$. The form of the anisotropic thermal ellipsoid is $\exp\{-[\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk]\}$.

	x	y	z	β_{11} (B, Å^2)	β_{22}	β_{33}	β_{12}
N(1)	−281 (6)	321 (3)	$\frac{1}{4}$	95 (7)	48 (2)	233 (11)	3 (3)
C(2)	731 (6)	1219 (3)	$\frac{1}{4}$	126 (8)	41 (2)	205 (11)	7 (4)
N(3)	2776 (4)	1119 (3)	$\frac{1}{4}$	106 (6)	31 (2)	362 (12)	−16 (3)
C(4)	3743 (5)	199 (3)	$\frac{1}{4}$	37 (7)	43 (2)	226 (11)	3 (3)
C(5)	2456 (6)	−711 (3)	$\frac{1}{4}$	123 (8)	35 (2)	196 (10)	−2 (4)
N(6)	575 (5)	−628 (2)	$\frac{1}{4}$	128 (8)	43 (2)	244 (10)	5 (3)
C(7)	3367 (11)	−1743 (4)	$\frac{1}{4}$	243 (14)	32 (3)	398 (22)	23 (5)
O(2)	−70 (4)	2052 (2)	$\frac{1}{4}$	152 (7)	47 (2)	462 (13)	37 (3)
O(4)	5586 (4)	151 (2)	$\frac{1}{4}$	94 (6)	69 (2)	369 (11)	−13 (3)
H(1)	−1516 (61)	351 (24)	$\frac{1}{4}$	1·2 (7)			
H(3)	3257 (70)	1750 (35)	$\frac{1}{4}$	4·1 (11)			
H(71)	2517 (80)	−2219 (46)	$\frac{1}{4}$	5·4 (16)			
H(72)	4208 (71)	−1822 (27)	1440 (62)	7·1 (11)			

respectively, based on the 513 observations and 102 variables. This apparent improvement in R_2 is not significant at the 1 % confidence level (Hamilton, 1965) and all discussion in this paper is based on the model obtained from the centrosymmetric refinement. The positional and thermal parameters derived from this last cycle of least-squares refinement, with their associated standard deviations as estimated from the inverse matrix, are given in Table 1.*

A final difference map contained one peak of height 0·56 e Å^{-3} in the plane of the molecule and approximately 0·8 Å from oxygen atom O(2); no other peak exceeded 0·27 e Å^{-3}.

Discussion. The aza analogs of pyrimidines and purines are of considerable interest because some of them are anti-neoplastic or funtistatic agents (Skoda, 1963; Bennett & Montgomery, 1967); specifically, 6-azathymine has been shown to inhibit the growth of the bacterium *S. Faecalis* (Prusoff & Welch, 1956). This biological activity has been ascribed to potentially severe differences between the hydrogen bonding, base pairing and electronic properties of the azapyrimidine and those of the parent pyrimidine, as well as to changes in the relative orientations of the base and the sugar in the related azapyrimidine nucleoside (Donohue & Trueblood, 1960; Haschemeyer & Rich, 1967; Schwalbe & Saenger, 1973; Singh & Hodgson, 1974*a*, *b*).

In the centrosymmetric space group *Pnam*, the azapyrimidine ring is constrained to planarity; a view of the molecule, including the bond angles, is shown in Fig. 1. The bond lengths in 6-azathymine are compared with those of thymine (Ozeki, Sakabe & Tanaka, 1969) and of 6-azauracil (Singh & Hodgson, 1974*c*) in Table 2. The bond lengths and angles in 6-azathymine are, as anticipated, more similar to those of 6-azauracil than to those of thymine or of uracil (Stewart & Jensen, 1967). It is noteworthy, however, that in 6-azathymine the N(1)–N(6) bond apparently contains even less double-bond character than in 6-azauracil, which in turn contains less than the N(1)–C(6) bond in uracil. Moreover, the carbonyl bonds C(2)–O(2) and C(4)–O(4) are apparently unequal in 6-azathymine, with C(2)–O(2) shorter than C(4)–O(4), while they are virtually equal in 6-azauracil; in thymine, C(2)–O(2) is longer than C(4)–O(4).

The hydrogen bonding in 6-azathymine is quite extensive, with all available donor and acceptor atoms except N(6) participating in intermolecular hydrogen bonding; the probable hydrogen bonds are tabulated in Table 3. The hydrogen bonding leads to an arrangement in which the molecules form an infinite chain along the crystallographic *a* axis, the chain being formed by N(1)–H(1)···O(4) hydrogen bonds of length 2·791 Å. As is shown in Fig. 2, the chains are linked to each other through N(3)–H(3)···O(2) intermolecular hydrogen bonds of length 2·790 Å to molecules which are related by the *a* glide, so that the overall result is a

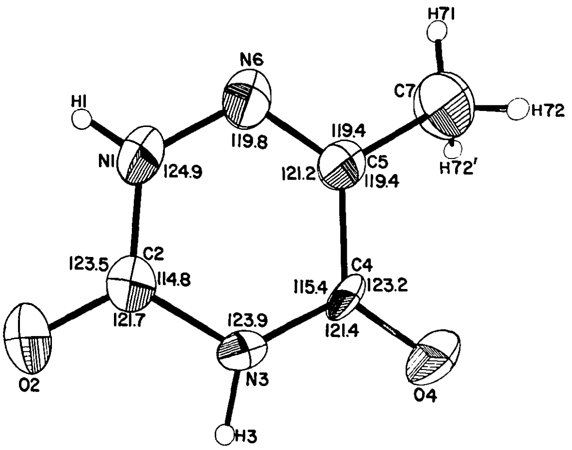

Fig. 1. View of the 6-azathymine molecule showing the bond angles (not involving hydrogen atoms) and the atomic numbering scheme. The thermal ellipsoids of the hydrogen atoms have been artificially reduced for clarity. Estimated standard deviations on angles are 0·3–0·4°.

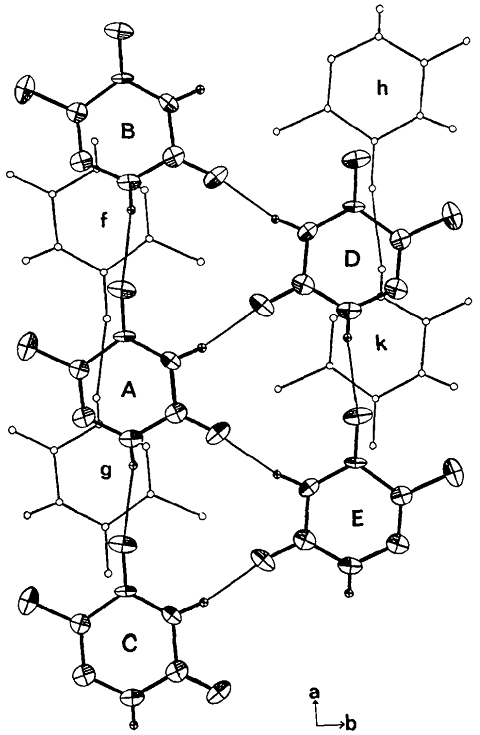

Fig. 2. View of the hydrogen bonding and sheet structure in 6-azathymine. Rings *A–E*, drawn with thicker bonds and 50 % probability ellipsoids, are in one sheet, while rings *f–k* are in the sheet below. The minimal overlap between molecules in adjacent sheets is apparent from this view. Rings *B* and *C* are related to the reference molecule (*A*) by translation along the *a* axis, ring *D* is related to *A* by the **a** glide, and ring *E* is related to *D* by translation along **a**. The methyl hydrogen atoms have been omitted for clarity.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31133 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Intramolecular distances in 6-azathymine (6AT) thymine (T), and 6-azauracil (6AU), in* Å

	6AT	T[a]	6AU[b]
N(1) -C(2)	1·354 (5)	1·31 (2)	1·366 (3)
C(2)—N(3)	1·383 (5)	1·35 (2)	1·378 (2)
N(3) -C(4)	1·365 (4)	1·41 (2)	1·359 (2)
C(4)—C(5)	1·470 (5)	1·48 (2)	1·456 (2)
C(5)—N(6)[c]	1·271 (5)	1·37 (2)	1·291 (2)
N(6)[c]-N(1)	1·365 (5)	1·41 (2)	1·351 (3)
C(5)—C(7)	1·479 (6)	1·52 (2)	—
C(2)—O(2)	1·213 (5)	1·25 (2)	1·224 (2)
C(4)—O(4)	1·242 (5)	1·19 (1)	1·224 (2)
N(1) -H(1)	0·83 (4)	*d*	1·02 (3)
N(3) -H(3)	0·88 (5)	*d*	0·92 (3)
C(7)—H(71)	0·84 (6)	*d*	—
C(7)—H(72)	0·88 (4)	*d*	—

(*a*) Data from Ozeki *et al.* (1969). (*b*) Data from Singh & Hodgson (1974*c*). (*c*) C(6) in thymine. (*d*) H atoms were not located.

Table 3. *Probable intermolecular* A–H$\cdots B$ *hydrogen bonds*

A	H	B	$A\cdots B$ (Å)	H$\cdots B$ (Å)	A–H$\cdots B$ (°)
N(1)	H(1)	O(4)	2·791 (5)	1·97 (4)	170 (3)
N(3)	H(3)	O(2)	2·790 (4)	1·93 (5)	166 (4)

sheet-like structure which is perpendicular to the *c* axis; neighboring sheets are separated by 3·17 Å, or one-half of the *c* axis length. The shortest interatomic distances between molecules in adjacent sheets are N(1)–N(6) and C(4)–O(4) separations of 3·20 and 3·23 Å, respectively. As can be seen in Fig. 2, there is evidently very little overlap between the individual molecules in the adjacent sheets.

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Vanadium Oxychloride

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Abstract. VOCl, orthorhombic, *Pmmn*, $a=3{\cdot}780$ (5), $b=3{\cdot}300$ (5), $c=7{\cdot}91$ (1) Å, $V=98{\cdot}67$ Å^3, $Z=2$, $D_c=$ 3·45 g cm^{-3}. Final R 0·091 for 491 reflexions. VOCl is isotypic with FeOCl and TiOCl.

Introduction. VOCl was prepared by the reaction of VCl_3 with V_2O_3. Single crystals were obtained by transport over the vapour phase in a temperature gradient using the method of Schäfer & Wartenpfuhl (1961). X-ray diffraction diagrams of VOCl powder are known from the work of Ehrlich & Seifert (1959) and have been indexed on the assumption that VOCl is isomorphous with TiOCl (Schäfer, Wartenpfuhl & Weise, 1958) and FeOCl (Goldsztaub, 1935). The indexing was based on the structure suggested by Goldsztaub.

In order to determine the structure of VOCl a plate-like single crystal with dimensions 0·20 × 0·06 × 0·005 mm was mounted in air with the rotation axis parallel to the plane of the plate. This direction proved to be that of the *b* axis. The unit-cell parameters $a=3{\cdot}78$, $b=3{\cdot}30$, $c=7{\cdot}91$ Å, $Z=2$ and the space group *Pmmn* were known from previous work by Schäfer & Wartenpfuhl (1961) and by Ehrlich & Seifert (1959) and were confirmed by our own X-ray investigation with photographic methods.

A Nonius CAD-4 four-circle automatic diffractometer and graphite-monochromated Mo $K\alpha$ radiation