corresponding bond lengths found in the above-mentioned structures [1·487 (4), 1·508 (4) and 1·509 (8) Å].

The polarization of the S=O(3) bond enhances the participation of O(3) as an acceptor, and that of C(20), which is attached to S, as a donor in the formation of the intermolecular C—H···O=S bond. The H(20,3)···O(3′) distance is 2·29 (4) Å, C(20)—H(20,3)···O(3′) 137 (3)° and C(20)—H(20,3) 1·02 (4) Å. These values lie in the middle of the range of those compiled for a number of C—H···O bonds (Taylor & Kennard, 1982). The molecules joined by these bonds form chains along the *b* axis. The next shortest intermolecular contact is H(22,2)···H(22,3′) = 2·32 (5) Å and all other H···H contacts are ≥ 2·48 Å.

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Structure of 5-Methyl-2-thiocytosine Hemihydrate

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Abstract. $C_5H_7N_3S.\frac{1}{2}H_2O$, $M_r = 150\cdot2$, orthorhombic, $P2_12_12$, $a = 9\cdot9233\,(4)$, $b = 12\cdot9693\,(8)$, $c = 5\cdot4094\,(3)$ Å, $V = 696\cdot18\,(6)$ Å^3, $Z = 4$, $D_m = 1\cdot42$, $D_x = 1\cdot433$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot7107$ Å, $\mu = 0\cdot333$ mm^{-1}, $F(000) = 316$, $T = 297$ K, $R = 0\cdot049$ for 1565 observed reflections. The sulfur atom acts as an acceptor of N—H···S and O*W*—H···S hydrogen bonds. The water oxygen sits on a twofold axis along **c** and acts as a donor of two symmetry-related O*W*—H···S hydrogen bonds and at the same time acts as an acceptor of two symmetry-related N—H···O*W* hydrogen bonds. The environment around O*W* is nearly tetrahedral.

Introduction. Methylated cytosine derivatives like 5-methylcytosine and 5-methyl-2-thiocytosine (5M2TC) are of considerable biological importance, since they have long been known to be definite constituents of DNA and RNA (Rink, 1974). Some of these cytosine derivatives seem to regulate nucleic-acid structures by affecting base-pair formation as exemplified in the clover-leaf arrangement of tRNA (Inose, Miyata &

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Iwanami, 1972). Further, experimental evidence suggests that RNA methylation is altered in tumour tissues (Tsutsui, Srinivasan & Borek, 1966). The process of methylation of nucleic acids is an important event during the course of chemical carcinogenesis and is brought about by a suitable methylating agent. In this context, the structure determination of 5M2TC was undertaken as part of a project on modified nucleic acid bases of biological importance. The crystal structure of another modified nucleic acid base, 6-amino-2-thiouracil monohydrate (6A2TU), has been reported (Swaminathan & Chacko, 1978).

Experimental. Sample of 5M2TC from Sigma Chemical Company, USA, pale-yellow crystals from aqueous solution, crystal size 0·25 × 0·30 × 0·45 mm, density measured by flotation in benzene/bromoform, Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, 25 reflections ($12 < 2\theta < 18°$) used for measuring lattice parameters, no absorption correction, $2\theta_{\max} = 70°$, index range $0 < h < 16$, $0 < k < 20$, $0 < l < 8$, standard reflections and their e.s.d.'s: 380 (0·24%), 181 (0·09%), 272 (0·92%), 1774 reflections measured, 1565 reflections with $I > 3\sigma(I)$, structure solution using *MULTAN*80 (Main *et al.*, 1980), least-squares refinement minimizing $\sum w(|F_o|-|F_c|)^2$, $w = 1$ for all reflections, *SHELX*76 (Sheldrick, 1976), anisotropic temperature factors for non-hydrogen atoms, hydrogen atoms from difference Fourier map and refined, final $R = wR = 0{\cdot}049$ for observed reflections, ratio of max. least-squares shift to e.s.d. in final refinement cycle = 0·2, max. and min. heights in final difference Fourier synthesis = 0·33 and −0·27 e Å^{-3} respectively, atomic scattering factors from *International Tables for X-ray Crystallography* (1974), calculations performed on an IBM 370 computer.

Discussion. Atomic parameters are given in Table 1.[*]

The bond lengths and angles in 5M2TC (Fig. 1) are in general agreement with those reported for 5-methylcytosine (5MC) (Takenaka, Kato & Sasada, 1980), 2-thiocytosine (2TC) (Furberg & Jensen, 1970), cytosine (McClure & Craven, 1973) and the average values in cytosine structures (Voet & Rich, 1970), except for small deviations. The slight deviation in bond lengths and angles of 5M2TC from the 2TC values may be attributed to the steric and electronic effects caused by methylation. The electron-releasing methyl group attached to C(5) makes the C(4)—C(5)—C(6) angle [116·0 (3)°] slightly smaller as compared to that in cytosine [117·0 (2)°]. This is accompanied by a small lengthening of the C(5)—C(4) and C(5)—C(6) bonds in comparison to cytosine which is due to the repulsion between the methyl hydrogen atoms attached to C(7) and the hydrogen atoms of N(4) or C(6) atoms. This is analogous to the interpretation of benzene-ring deformation on the basis of the valence-shell electron pair repulsion theory (Domenicano, Vaciago & Coulson, 1975). A comparison of the bond parameters in 5M2TC with the average values for cytosine (Donohue,

Table 1. *Fractional atomic coordinates of non-hydrogen atoms (×10^4) and hydrogen atoms (×10^3) and their isotropic thermal parameters (×10^2) with their e.s.d.'s in parentheses*

$$B_{\rm eq} = \tfrac{4}{3}(B_{11}a^2 + B_{22}b^2 + B_{33}c^2).$$

	x	y	z	$B_{\rm eq}/B_{\rm iso}$(Å^2)
N(1)	996 (3)	2731 (3)	1212 (8)	250
C(2)	2235 (4)	2362 (3)	525 (8)	240
N(3)	3350 (3)	2722 (3)	1631 (8)	237
C(4)	3227 (4)	3388 (3)	3520 (9)	220
N(4)	4357 (3)	3715 (3)	4622 (8)	285
C(5)	1944 (4)	3763 (3)	4356 (9)	243
C(6)	862 (4)	3418 (4)	3116 (10)	273
C(7)	1838 (5)	4486 (4)	6513 (11)	328
S	2329 (1)	1443 (1)	−1734 (2)	289
O*W*	5000	5000	8924 (9)	298
H(O*W*)	560 (4)	465 (4)	1009 (9)	237
H(N1)	21 (5)	244 (4)	41 (9)	243
H(1N4)	442 (5)	423 (4)	583 (10)	228
H(2N4)	530 (5)	357 (4)	424 (9)	228
H(C6)	−3 (5)	362 (4)	345 (9)	260
H(1C7)	85 (9)	457 (4)	695 (10)	279
H(2C7)	224 (5)	421 (4)	809 (10)	279
H(3C7)	204 (5)	514 (4)	606 (9)	279

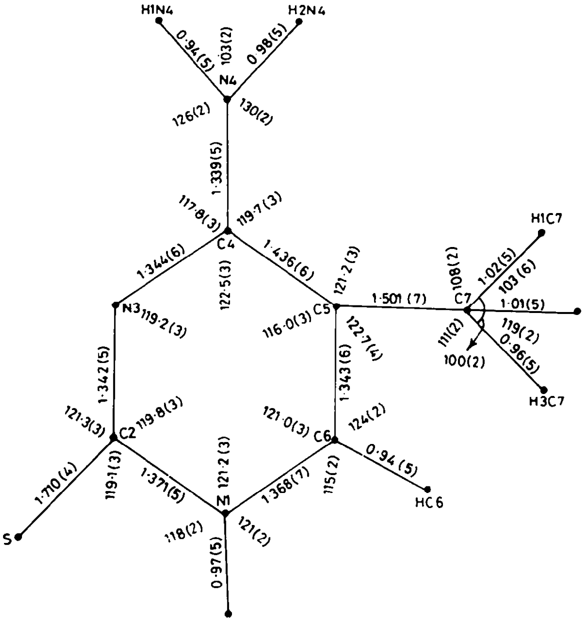

Fig. 1. Bond lengths (Å) and angles (°) in 5M2TC.

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[*] Lists of structure factors, anisotropic thermal parameters and a least-squares-plane calculation have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42283 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1968) shows significant differences in the region of atom C(2) to which the sulfur atom is attached, which is as expected. The C(2)=S bond length of 1·710 (4) Å has apparently less double-bond character than the C=O bond in cytosine [1·241 (3) Å]. The adjacent ring bonds C(2)—N(3) and C(2)—N(1) in 5M2TC have the values 1·342 (5) and 1·371 (5) Å respectively, which are slightly shorter than the corresponding average values of 1·358 (5) and 1·389 (13) Å respectively in cytosines. These changes may be interpreted in terms of flow of bonding electrons from the neighbouring C(2)—N(3) and C(2)—N(1) bonds to the external double bond on substitution of the sulfur atom by oxygen. This flow of bonding electrons may be attributed to the higher electronegativity of oxygen in comparison with sulfur. The C(2)—N(1)—C(6) angle of 121·2 (3)° is larger than 120° and it confirms the presence of a hydrogen atom to N(1) (Singh, 1965). A least-squares-plane calculation* shows that although the pyrimidine ring is planar within ±0·015 (4) Å the sulfur atom is out of plane by 0·127 (2) Å.

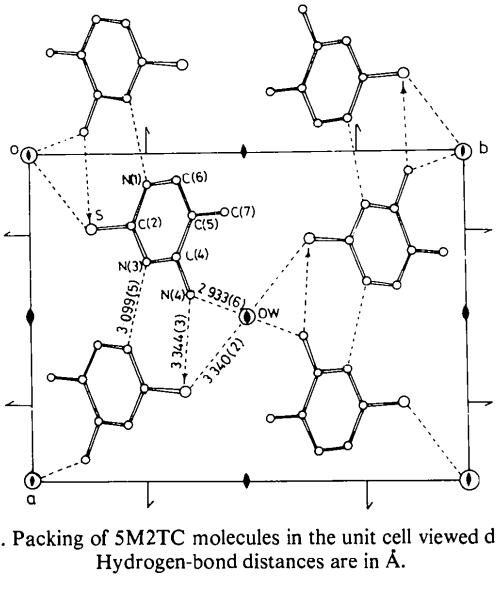

Fig. 2. Packing of 5M2TC molecules in the unit cell viewed down **c**. Hydrogen-bond distances are in Å.

Table 2. *Intermolecular hydrogen-bond distances and angles*

E.s.d.'s are in parentheses. *D*: donor, *A*: acceptor.

D—H···*A*	*D*···*A* (Å)	H···*A* (Å)	*D*—H···*A* (°)
N(1)—H(N1)···N(3^{i})	3·099 (5)	2·16 (5)	162 (3)
N(4)—H(2N4)···S^{ii}	3·344 (3)	2·43 (5)	156 (3)
N(4)—H(1N4)···O*W*	2·932 (6)	2·03 (5)	160 (3)
O*W*—H(O*W*)···S^{iii}	3·340 (2)	2·40 (5)	161 (3)

Symmetry code: (i) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, -z+1$.

Fig. 2 shows the packing of 5M2TC in the unit cell with the hydrogen-bonded contacts (Table 2) shown as dashed lines. The hydrogen atom attached to N(1) forms an N—H···N hydrogen bond with a symmetry-related N(3) atom, of length 3·099 (5) Å. The amino hydrogen atoms attached to N(4) enter into strong hydrogen-bonded interactions with O*W* and a symmetry-related sulfur atom, of lengths 2·933 (6) and 3·340 (2) Å respectively. It is interesting to note that the sulfur atom acts as an acceptor of two hydrogen bonds N—H···S and O*W*—H···S. The hydrogen-bond distances of these two hydrogen bonds involving sulfur agree fairly well with the range of values observed by Srinivasan & Chacko (1967) in structures containing N—H···S and O—H···S hydrogen bonds with sulfur as the acceptor atom. O*W* has a nearly tetrahedral coordination. It is located on the twofold axis of symmetry and it acts as a donor of two hydrogen bonds to two sulfur atoms related by a twofold symmetry and at the same time accepts two hydrogen bonds from two symmetry-related amino nitrogen atoms. However, the O*W*—H···S distance of 3·340 (2) Å is significantly shorter than the value of 3·49 (1) Å reported for 6A2TU, which indicates that the O*W*···S interaction is stronger in 5M2TC than in 6A2TU.

The N(1)—H···N(3) and the N(4)—H···S hydrogen bonds link the molecules to form a ribbon extended along the **a** direction. The water molecular link the adjacent ribbons with N(4)—H···O*W* and O*W*—H···S hydrogen bonds.

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* See deposition footnote.

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2,6-Bis[(2-phenyl-1,3-dioxolan-2-yl)methyl]pyridine

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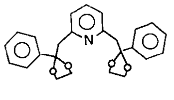
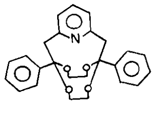
Abstract. $C_{25}H_{25}NO_4$, $M_r = 403{\cdot}5$, monoclinic, $C2/c$, $a = 21{\cdot}192\,(6)$, $b = 6{\cdot}276\,(2)$, $c = 15{\cdot}845\,(5)$ Å, $\beta = 95{\cdot}29\,(3)°$, $V = 2098\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}277$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}81$ cm^{-1}, $F(000) = 856{\cdot}0$, $T = 296$ K, $R = 0{\cdot}041$ for 1273 observations. The molecule has crystallographic symmetry 2. The planar pyridine and phenyl rings [maximum deviations 0·005 (2) Å for each] form a dihedral angle of 55·0 (2)°, and the acetal ring is in the envelope conformation with an O atom at the flap. The crystal packing is dominated by the parallel stacking of aromatic rings.

Introduction. The title compound was prepared during a study of the chelation properties of a series of bis(ethyleneglycol) acetals of 2,6-diacylpyridine. The synthetic procedure afforded one of two possible isomers: the bis(acetal) (I) or the cryptand (II).



(I)



(II)

Standard spectral means (NMR, IR, MS) were insufficient to distinguish between the two structures, and thus a crystal-structure determination was conducted. This investigation proved isomer (I) to be correct.

Experimental. Yellow crystal, dimensions 0·20 × 0·23 × 0·60 mm, cut from a needle, space-group determination from systematic absences hkl with $h + k$ odd, $h0l$ with l odd and successful refinement in centrosymmetric space group. Cell dimensions from least squares of setting angles of 25 reflections, $13 < \theta < 14°$. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator. Intensity data by ω–2θ scans designed to yield $I = 50\sigma(I)$, scan rates varied 0·26–5·0° min^{-1}. Data having $1 < \theta < 25°$, $h + k$ even, $0 \le h \le 26$, $0 \le k \le 7$, $-18 \le l \le 18$ measured, corrected for Lorentz, polarization, background. Absorption and decay insignificant (600, 020, 0,0,10 standard reflections, 3·2% variation). Equivalent data averaged, $R_{\text{int}} = 0{\cdot}027$, 1841 unique data. Structure solved using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), refined by full-matrix least squares based on F using 1273 data with $I > 3\sigma(I)$, $w = [\sigma^2(|F|) + 0{\cdot}02|F|^2]^{-1}$, using *SHELX*76 (Sheldrick, 1976) and Enraf–Nonius *SDP* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974). Non-H atoms anisotropic; H atoms located by ΔF map, refined isotropically (those of acetal groups: fixed contributions, C–H 0·95 Å, $B = 8{\cdot}0$ Å^2). Final $R = 0{\cdot}041$ (0·074 all data), $wR = 0{\cdot}060$, $S = 1{\cdot}994$ for 172 variables. Max. $\Delta/\sigma < 0{\cdot}01$ in final cycle, max. residual density 0·16 e Å^{-3}, min. −0·18 e Å^{-3}, extinction $g = 1{\cdot}3\,(2) \times 10^{-6}$ $[|F_c| = |F_o|(1 + gI_c)]$.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 1.* Bis(acetal) (I) possesses crystallographic C_2 symmetry. Both pyridine and phenyl rings are planar [maximum deviations 0·005 (2) Å for each], and they form a dihedral angle of 55·0 (2)°. The conformation of (I) in the crystal is illustrated in Fig. 1 and is specified by torsion angles N–C(3)–C(4)–C(5) −113·8 (3),

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42290 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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