of each molecule are inclined at angles of 77·5 and 63·9°. The sp^2–sp^2 linking bond is of comparable length to that found in 8,8'-biquinolyl, 1·495 (2) Å (Lenner & Lindgren, 1976), where the molecular halves are inclined at an angle of 96·8°. The conformation of the present molecule and of 8,8'-biquinolyl effectively prevents overlap of π orbitals and there would thus seem to be no π contribution to this bond. Comparable bonds in the completely planar perylene, 1·471 (5) Å (Camerman & Trotter, 1964), and in a perylene fluoranil complex, 1·473 (5) Å (Hanson, 1963), are significantly shorter.

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3-Methylcytosine Hemihydrate: The Aminooxo Tautomer

By T. Srikrishnan, P. K. Sengupta* and R. Parthasarathy†

Center for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, NY 14263, USA

Abstract. $C_5H_7N_3O \cdot \frac{1}{2}H_2O$, FW 134, orthorhombic, *Pba*2, $a = 8 \cdot 132$ (2), $b = 13 \cdot 333$ (2), $c = 5 \cdot 976$ (1) Å ($t = 22 \pm 3$°C), D_m (flotation) $= 1 \cdot 37$, $D_x = 1 \cdot 36$ g cm⁻³, $Z = 4$, μ(Cu $K\alpha$) $= 6 \cdot 5$ cm⁻¹, $F(000) = 284$, λ(Cu $K\alpha$) $= 1 \cdot 54051$ Å, $R = 0 \cdot 06$ for 763 reflections. The cytosine moiety exhibits the aminooxo form in the solid state with no H atom on N(1). The water molecules lie on twofold axes. The structure consists of layers of molecules joined by N—H···N and N—H···O hydrogen bonds. There is only partial stacking of the cytosine rings in the crystal structure.

Introduction. The crystal structure of 3-methylcytosine (m^3cyt) was undertaken to study its tautomerism and its hydrogen bonding. Crystals of m^3cyt were grown by slow evaporation from a methanol–water mixture as well formed square plates. A crystal $0 \cdot 3 \times 0 \cdot 35 \times 0 \cdot 35$ mm was used for data collection. The crystals are orthorhombic and the space group, as deduced from the systematic absences ($0kl$, k odd; $h0l$, h odd), could be *Pba*2 or *Pbam*. The refined unit-cell parameters and

other cell data are in the *Abstract*. Three-dimensional intensities were collected on a GE XRD-6 diffractometer, using a 5° take-off angle, by the stationary-crystal–stationary-counter technique (Furnas & Harker, 1955). Ni–Co balanced filters were used for monochromatization. 885 reflections were measured, of which 122 had intensities less than twice the background in that $\sin\theta/\lambda$ range. The difference in absorption as a function of φ was measured for the axial reflections and this was used for correcting for absorption. Lorentz and polarization corrections were applied and the data were processed in the usual way.

The crystal structure was solved by the application of the multisolution technique using *MULTAN* (Germain, Main & Woolfson, 1971). After futile attempts to solve the structure in the centrosymmetric (as suggested by the near centric distribution of normalized structure factors) space group *Pbam*, the structure was obtained readily from the noncentrosymmetric space group *Pba*2 and refined by a least-squares procedure with block-diagonal approximation. The water O atoms lie on twofold axes. The location of the water H atoms is not accurate. All the other H atoms were refined isotropically and the non-hydrogen anisotropically. The

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* On leave from Memphis State University, Memphis, Tennessee.
† To whom correspondence should be addressed.

Table 1. *Final atomic coordinates* (×10⁴) *with e.s.d.'s in parentheses*

	x	y	z
O(2)	1117 (6)	3300 (3)	4992 (9)
OW	0*	5000*	3170 (9)
N(1)	2592 (6)	3782 (3)	8039 (9)
N(3)	2249 (5)	2064 (3)	7087 (8)
N(4)	3255 (6)	779 (3)	9366 (9)
C(2)	1955 (6)	3092 (3)	6661 (9)
C(4)	3076 (6)	1752 (3)	8930 (9)
C(5)	3721 (6)	2480 (4)	10393 (9)
C(6)	3430 (7)	3465 (4)	9825 (12)
C(M3)	1569 (7)	1319 (4)	5527 (10)

* Atom on the diad axis at (0, ½, z).

Table 2. *Final atomic coordinates* (×10³) *for the* H *atoms with e.s.d.'s in parentheses*

	x	y	z
H1(N4)	320 (6)	49 (4)	873 (10)
H2(N4)	398 (9)	46 (5)	1048 (14)
H1(M3)	35 (12)	87 (6)	608 (17)
H2(M3)	266 (9)	82 (5)	489 (14)
H3(M3)	112 (10)	152 (6)	424 (18)
H(C5)	442 (8)	230 (5)	1158 (12)
H(C6)	396 (11)	416 (6)	1074 (16)

Fig. 1. Bond distances (Å) and angles (°) in 3-methyl-cytosine.½H₂O

final R value is 0·060 for the 763 reflections (I > 2σ). Scattering factors are those in *International Tables for X-ray Crystallography* (1968), except for H (Stewart, Davidson & Simpson, 1965). The final atomic coordinates are given in Tables 1 and 2.*

Discussion. The distances and angles in the molecule are given in Fig. 1. The average e.s.d.'s for the bond

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33181 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 2. Tautomers of 3-methylcytosine: (a) aminooxo, (b) iminooxo and (c) iminohydroxy forms.

Fig. 3. Stereodiagram to illustrate the partial stacking of cytosine rings in the crystal structure.

distances and angles are 0·006 Å and 0·4° respectively for the non-hydrogen atoms and 0·08 Å and 5° for the H atoms.

Formally, three neutral tautomeric structures can be written for m³cyt (Fig. 2). Comparison of the distances and angles (Fig. 1) of m³cyt with those of cytosine and cytosine.H₂O (McClure & Craven, 1973) and protonated cytosine (see Table 2 of Mandel, 1977), the lack of an H atom on N(1), and the hydrogen-bonding pattern (Fig. 4a) all show that the molecule exists as the aminooxo tautomer. It has been pointed out (Dreyfus, Bensaude, Dodin & Dubois, 1976) from spectral and thermodynamic studies that m³cyt exists mainly as the 1(H)-aminooxo tautomer in water, but as a mixture of two tautomers, the aminooxo form and the iminooxo form, in non-polar solvents.

The cytosine ring is slightly puckered with C(2), N(3) and N(4) deviating from the mean plane of the other atoms by −0·019, 0·024 and −0·037 Å respectively. There is only a partial stacking of the cytosine rings in the structure, as can be seen from the stacking diagram given in Fig. 3.

Details of the hydrogen-bonding scheme are given in Table 3. The amino group takes part in two hydrogen bonds: N—H···N(1) with N(1) as the acceptor and N—H···OW with the water O atom as the acceptor. The angle between the planes of the bases which form the N—H···N(1) hydrogen bonds is 64°. Similar hydrogen-bonding patterns in which the hydrogen-bonded nucleic-acid bases are inclined to one another

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

D–H$\cdots A$	D–H	H$\cdots A$	$D\cdots A$	$\angle D$–H$\cdots A$
N(4)–H1(N4)$\cdots$N(1^i)	0.54 (5)	2.41 (6)	2.863 (4)	143 (8)
N(4)–H2(N4)$\cdots$OW^{ii}	0.99 (17)	1.95 (14)	2.875 (4)	168 (12)

Superscripts refer to the following symmetry-related positions: (i) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 + z$.
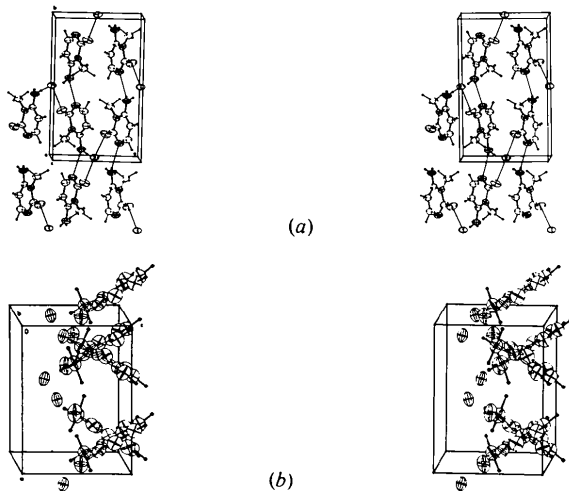

(a)

(b)

Fig. 4. Stereoscopic views of the packing in the structure: (a) view down (001), (b) view down (010).

have been observed earlier in 5-nitro-6-methyluracil (Parthasarathy & Srikrishnan, 1977) and in 5-chlorouridine (Hawkinson & Coulter, 1971). The water molecule is hydrogen-bonded to two carbonyl O atoms (2.674 Å). The packing of the molecules in the crystal structure is given in the two stereodiagrams (Fig. 4).

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Hexamethylenetetramine Oxide–Hydrogen Peroxide–Water (1:1:1)

By Thomas C. W. Mak and Yiu-Shing Lam

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

Abstract. $(CH_2)_6N_4O.H_2O_2.H_2O$, monoclinic, space group $P2_1/c$, $a = 6.374$ (5), $b = 9.538$ (5), $c = 16.84$ (1) Å, $\beta = 103.57$ (8)°, $Z = 4$, $D_m = 1.40$ (1) (by flotation in hexane/CCl$_4$), $D_x = 1.390$ g cm^{-3}. The structure was determined from film data and refined to $R = 0.124$. The O atoms of the three molecular components are linked by hydrogen bonds to form corrugated layers normal to **c**. Neighboring layers, related by the c glide, pack with protruding $(CH_2)_6N_4$ groups fitting into hollows between the layers.