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) $\frac{1}{2} + x, \frac{1}{2} - y, 1 + z$.
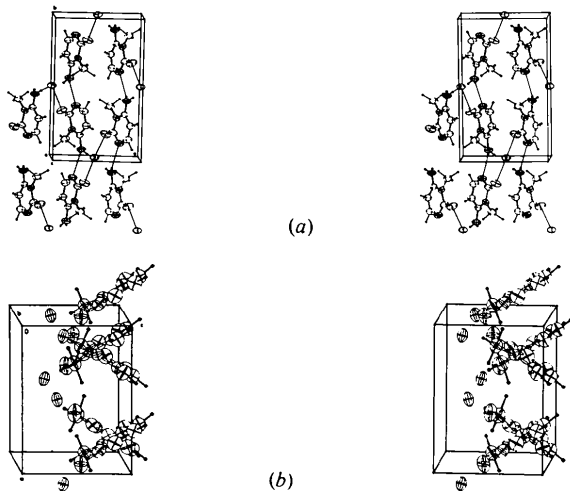

(a)

(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)

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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.

Introduction. It has been shown that hexamethylene-tetramine, $(CH_2)_6N_4$, reacts with 30% H_2O_2 to give two crystalline adducts, $(CH_2)_6N_4O.H_2O_2.H_2O$ and $(CH_2)_6N_4O.HCOOH$ (Lam & Mak, 1978a). The structure of the formic acid adduct of hexamethylene-tetramine oxide has been determined (Lam & Mak, 1978b). In the present work, the monohydrated H_2O_2 adduct was subjected to analysis to elucidate the nature of the molecular association and to study the effect of a highly polar substituent, the N-oxide functional group, on the geometry of the heterocyclic ring system. It constitutes part of our current structural investigation of hydrogen-bonded molecular complexes of hexamethylenetetramine (Mak, Tse, Chong & Mok, 1977; Mak, Lau, Ladd & Povey, 1978) and its N-oxide (Lam & Mak, 1978b).

The crystalline adduct was prepared as described by Lam & Mak (1978a). The crystals were colorless thin prisms well developed on the (100) and (010) faces. As the compound is hygroscopic and decomposes at room temperature, the crystals were mounted in quartz capillaries filled with paraffin wax of low molecular weight and maintained at about 9 °C by cool air from a hose leading to the freezer compartment of a re-frigerator. Cell dimensions were determined from high-angle reflections on all three zero-layer Weissenberg photographs calibrated with superimposed NaCl pow-der lines and refined by minimizing the sum of the residuals $|\sin^2 \theta_m - \sin^2 \theta_c|$. Intensities were collected for $0kl–6kl$ and $h0l–h9l$ by the multiple-film equi-inclination Weissenberg method with Cu $K\alpha$ ($\lambda = 1.5418$ Å) radiation. Decomposition was quite notice-able after a day or two, and 10 roughly spherical crystals of mean diameter 0.7 mm were needed to collect all the data. The visually estimated intensities were corrected for Lorentz and polarization factors but not for absorption ($\mu = 10.0$ cm^{-1}). A set of scaled structure amplitudes was derived (Hamilton, Rollett & Sparks, 1965), which, after reduction, consisted of 1577 independent observed and 662 unobserved reflections.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) from 412 reflections with $E > 1.24$. Full-matrix isotropic and anisotropic least-squares refinement of all 14 non-hydrogen atoms yielded $R = 0.141$. The strong reflections 002, 01$\bar{2}$, 020, 10$\bar{2}$, 102, and 110 appeared to suffer from extinction and were given zero weight in subsequent calculations. The positions of all 12 methylene H atoms were then generated with the program *GHMC* (Mak, Mok & Tse, 1977). Inclusion of these with $B = 5.5$ Å^2 gave a final R of 0.124. A difference map was feature-less and did not reveal the remaining H atoms.

Scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallog-raphy* (1974), and that for H from Stewart, Davidson

Table 2. *Bond angles* (°) *with e.s.d.'s in parentheses*

Around quaternary N atom (average O–N–C = 110.9, C–N–C = 108.0)

O(1)–N(1)–C(1)	111.8 (3)	C(1)–N(1)–C(2)	108.1 (3)
O(1)–N(1)–C(2)	110.2 (3)	C(1)–N(1)–C(3)	107.3 (3)
O(1)–N(1)–C(3)	110.6 (3)	C(2)–N(1)–C(3)	108.6 (3)

Around tertiary N atoms (average C–N–C = 109.4)

C(1)–N(2)–C(4)	110.8 (4)	C(4)–N(3)–C(5)	107.0 (3)
C(1)–N(2)–C(6)	112.4 (4)	C(3)–N(4)–C(5)	105.6 (3)
C(4)–N(2)–C(6)	107.9 (4)	C(3)–N(4)–C(6)	111.4 (4)
C(2)–N(3)–C(4)	111.6 (4)	C(5)–N(4)–C(6)	110.8 (4)
C(2)–N(3)–C(5)	107.1 (4)		

Around methylene C atoms (average N–C–N = 110.3)

N(1)–C(1)–N(2)	109.4 (4)	N(2)–C(4)–N(3)	111.3 (4)
N(1)–C(2)–N(3)	110.2 (4)	N(3)–C(5)–N(4)	112.4 (4)
N(1)–C(3)–N(4)	110.2 (4)	N(2)–C(6)–N(4)	108.0 (4)

Around O atoms

N(1)–O(1)···O(2)	116.3 (3)	O(2)–O(3)···O(4)^{iii}	103.4 (4)
N(1)–O(1)···O(3)^i	124.0 (3)	O(1)···O(4)···O(3)^{iv}	106.7 (2)
N(1)–O(1)···O(4)	115.9 (3)	O(2)···O(1)···O(4)	87.2 (2)
O(3)–O(2)···O(1)	105.6 (3)	O(2)···O(1)···O(3)^i	108.8 (2)
O(2)–O(3)···O(1)^{ii}	108.2 (3)	O(4)···O(1)···O(3)^i	97.1 (2)

Roman numerals refer to the following equivalent positions relative to the atom at x,y,z: (i) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

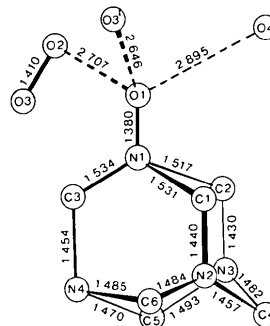|	x	y	z
O(1)	0.6887 (6)	0.2693 (4)	0.2225 (2)
N(1)	0.7201 (6)	0.2612 (4)	0.1443 (2)
N(2)	0.7397 (6)	0.1079 (4)	0.0314 (3)
N(3)	0.9712 (6)	0.3123 (4)	0.0607 (2)
N(4)	0.5809 (6)	0.3361 (4)	0.0024 (2)
C(1)	0.7081 (9)	0.1099 (5)	0.1133 (3)
C(2)	0.9397 (7)	0.3199 (5)	0.1419 (3)
C(3)	0.5464 (7)	0.3451 (5)	0.0846 (3)
C(4)	0.9491 (8)	0.1668 (5)	0.0291 (3)
C(5)	0.7958 (7)	0.3964 (5)	0.0074 (3)
C(6)	0.5715 (8)	0.1886 (6)	−0.0265 (4)
O(2)	0.7036 (8)	0.5291 (6)	0.2883 (3)
O(3)	0.5978 (8)	0.6175 (5)	0.2243 (3)
O(4)	1.0588 (10)	0.2012 (8)	0.3530 (4)

Fig. 1. Atom numbering and bond distances (Å). The e.s.d.'s of individual C–N, N–O, O–O and O···O distances are 0.006–0.007, 0.005, 0.007, and 0.006–0.008 Å respectively.

& Simpson (1965). Calculations were carried out on an ICL-1904A computer with *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, the weighting scheme being that of Cruickshank (1961) with $w = (2F_{min} + |F_o| + 2|F_o|^2/F_{max})^{-1}$, where F_{min} and F_{max} were 3·0 and 200·0 respectively.

The final atomic parameters are listed in Table 1.* Atom numbering and bond distances are shown in Fig. 1. Bond angles are listed in Table 2. A *PLUTO* (Motherwell, 1976) stereoplot of the molecular packing viewed along **b** is shown in Fig. 2.

Discussion. In the present adduct, the O atoms of all three molecular components are connected by hydrogen bonds to form corrugated layers normal to **c**. Each layer consists of infinite zigzag chains of alternating O(1) atoms (belonging to hexamethylenetetramine oxide molecules) and H_2O_2 molecules running parallel

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* Lists of structure factors, anisotropic temperature factors, and generated hydrogen positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33306 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

to **b**, adjacent chains being cross-linked by water molecules. Neighboring layers are related by the *c* glide, and the hexamethylenetetramine groups which protrude from both sides of each layer fit into hollows between the layers (Fig. 2). This layer structure may be contrasted with that of the 1:2 adduct of hexamethylenetetramine and thiourea (Mak, Lau, Ladd & Povey, 1978), in which hydrogen-bonded layers of N and S atoms are normal to **b** and neighboring ones related by the *c* glide. A stereoview of the stacking of three consecutive hydrogen-bonded layers is shown in Fig. 3. All available protons are utilized in hydrogen bonding, and their expected positions are indicated in Fig. 4. In this scheme, O(1) of the hexamethylenetetramine oxide molecule serves as proton acceptor in three hydrogen bonds, but none of the three tertiary N atoms are involved. In the H_2O_2 molecule, O(3) is involved in both donor and acceptor hydrogen bonding, whereas O(2) acts only as a proton donor. The water molecule forms two donor hydrogen bonds to O(1) and O(3), but its lone pairs are left intact. Comparison of measured O···O distances (Fig. 1) shows that H_2O_2 forms stronger hydrogen bonds than water. It is well established that the O–O bond of H_2O_2 is sub-
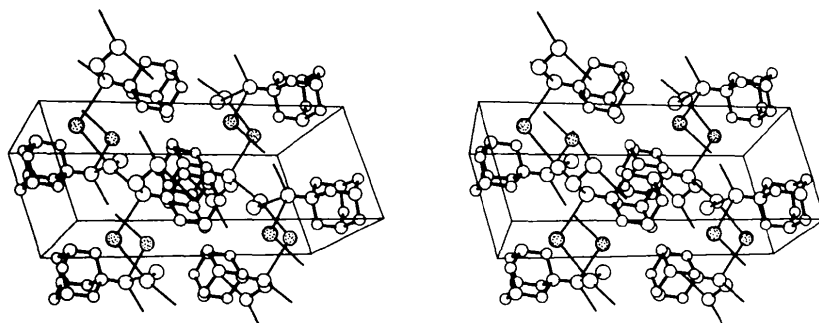

Fig. 2. Stereodrawing showing the molecular packing viewed approximately along **b** towards the origin of the unit cell at the lower left corner.
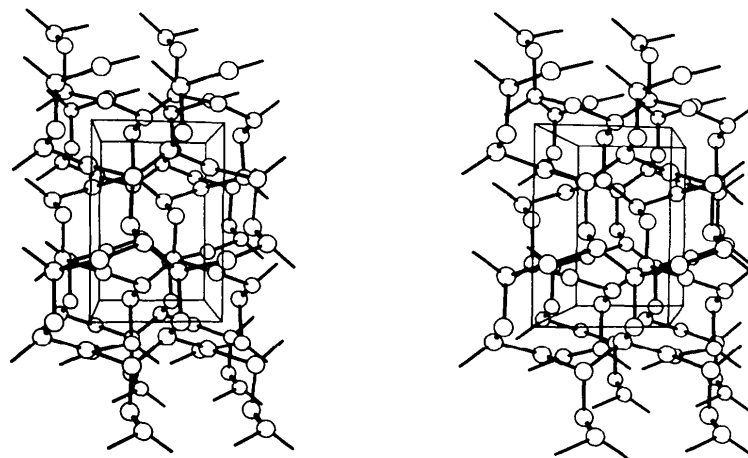

Fig. 3. Stereodrawing of three consecutive hydrogen-bonded layers viewed along **c**. The hexamethylenetetramine groups have been omitted for the sake of clarity.
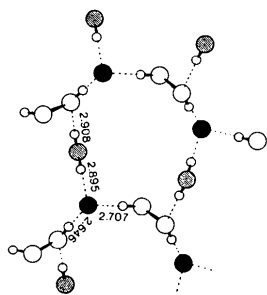
Fig. 4. Details of hydrogen bonding in a layer of O atoms showing the expected proton positions. O atoms belonging to hexamethylenetetramine oxide, water, and H_2O_2 molecules are indicated by successively lighter shades.

stantially shortened in crystals (Lu, Hughes & Giguère, 1941; Busing & Levy, 1965; Pedersen, 1967, 1969) compared to the vapor (Reddington, Olson & Cross, 1962). The O(2)–O(3) distance of 1·410 (7) Å is much shorter than reported peroxide bonds, in the range 1·44–1·48 Å, and this may be ascribed to the fact that the H_2O_2 molecule forms strong donor hydrogen bonds to two formally negative O(1) atoms in the crystal.

Since the diffraction data did not permit the location of H atoms, the O–O–H bond angle and the dihedral angle of the H_2O_2 molecule were estimated on the assumption that O–H bonds point in the same direction as O–H···O hydrogen bonds. The calculated angles are 106·9 (average) and 130·5° respectively. The deviation by ca 20° of the latter value from the corresponding angle of 111·5° in the gaseous molecule (Hunt, Leacock, Peters & Hecht, 1965) reflects the prevalence of optimum hydrogen bonding, which easily overcomes the rather low barrier to internal rotation.

In the 1:1 adduct of hexamethylenetetramine oxide and formic acid (Lam & Mak, 1978b), it has been shown that (i) the shortness of the N(1)–O(1) bond is in accord with the valence-bond formulation $\geqslant N^+–O^-$, (ii) the three types of C–N bonds disposed successively further away from the polar N-oxide function vary in the order long–short–normal relative to the C–N length in crystalline hexamethylenetetramine (Becka & Cruickshank, 1963), and (iii) the formally negative O(1) atom behaves like a lone pair on a tertiary N atom

in affecting cage geometry. The measured dimensions of the hexamethylenetetramine oxide molecule in the present adduct (Fig. 1 and Table 2) agree closely with corresponding values in the formic acid adduct and thus further substantiate the conclusions reached therein.

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