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Thymine hydrogen peroxide 0.55-solvate
0.45-hydrateAndrei V. Churakov^{a*} and Judith A. K. Howard^b^aN. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninskii prospect, Moscow 119991, Russian Federation, and^bDepartment of Chemistry, University of Durham, Science Laboratories, South Road, Durham DH1 3LE, England

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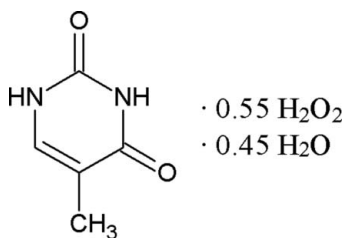
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Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; disorder in main residue; R factor = 0.045; wR factor = 0.108; data-to-parameter ratio = 11.8.

Thymine crystallizes from 50% hydrogen peroxide to give the title hydrogen peroxide water solvate, $\text{C}_5\text{H}_6\text{N}_2\text{O}_2 \cdot 0.55\text{H}_2\text{O}_2 \cdot 0.45\text{H}_2\text{O}$. The disordered peroxide and water molecules occupy the same positions. Thymine molecules are linked together by $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds forming chains parallel to the ac diagonal. Hydrogen peroxide molecules are combined by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds to give chains parallel to the c axis. Both kinds of chains are organized in a three-dimensional hydrogen-bonded network.

Related literature

For general background, see: Adams & Ramdas (1978); Churakov *et al.* (2005, 2006); Rojkind *et al.* (2002); Savariault & Lehmann (1980); Serra *et al.* (1992).



Experimental

Crystal data

 $\text{C}_5\text{H}_6\text{N}_2\text{O}_2 \cdot 0.55\text{H}_2\text{O}_2 \cdot 0.45\text{H}_2\text{O}$ $M_r = 152.93$ Monoclinic, $P2_1/c$ $a = 6.5047$ (16) Å $b = 19.194$ (5) Å $c = 5.6190$ (13) Å $\beta = 110.078$ (5)° $V = 658.9$ (3) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 0.13$ mm⁻¹ $T = 120$ (2) K

0.20 × 0.20 × 0.10 mm

Data collection

Bruker SMART 1K diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2003)

 $T_{\min} = 0.974$, $T_{\max} = 0.987$

4556 measured reflections

1733 independent reflections

1174 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.038$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.045$ $wR(F^2) = 0.108$ $S = 1.02$

1733 reflections

147 parameters

3 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.23$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1}-\text{H1} \cdots \text{O4}^{\text{i}}$	0.93 (4)	1.75 (4)	2.683 (3)	173 (5)
$\text{O12}-\text{H3} \cdots \text{O4}^{\text{i}}$	0.87 (5)	1.93 (5)	2.764 (4)	160 (5)
$\text{O2}-\text{H2} \cdots \text{O1}^{\text{ii}}$	0.97 (4)	1.52 (4)	2.446 (5)	159 (4)
$\text{O12}-\text{H4} \cdots \text{O1}^{\text{ii}}$	0.89 (5)	1.92 (5)	2.798 (5)	172 (6)
$\text{N1}-\text{H11} \cdots \text{O3}^{\text{iii}}$	0.82 (2)	2.01 (2)	2.8347 (18)	178.1 (18)
$\text{N2}-\text{H21} \cdots \text{O3}^{\text{iv}}$	0.93 (2)	1.90 (2)	2.8204 (18)	170.3 (18)

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

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2003); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2169).

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supplementary materials

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Thymine hydrogen peroxide 0.55-solvate 0.45-hydrate

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Comment

Hydrogen bonding plays the main role in forming crystals of peroxosolvates. It was supposed that it might be possible to design stable hydrogen peroxide carriers by maximizing the number of hydrogen bonds in the structure (Adams & Ramdas, 1978). Moreover, hydrogen peroxide complexes are of great importance for various biochemical processes (Rojkind *et al.*, 2002). Previously, the structure of adenine hydrogen peroxide adduct was determined (Serra *et al.*, 1992). Herein we report the structure of the title compound as part of our study of organic hydrogen peroxide solvates (Churakov *et al.*, 2005, 2006).

In the structure of the title compound, thymine molecules exhibit the expected planar molecular geometry (Fig. 1). Centrosymmetrically related thymine molecules are linked together by N1—H11 \cdots O3 and N2—H21 \cdots O3 (Table 1) hydrogen bonds forming chains parallel to *ac* diagonal (Fig. 2).

The H₂O₂ molecule has a skew conformation with H—O—O—H torsion angle equal to 113 (4)°. The O—O bond length (1.453 (4) Å) is somewhat shorter than that observed in crystalline hydrogen peroxide (1.461 (3) Å; Savariault & Lehmann, 1980). The disordered peroxide and water molecules occupy the same positions in the crystal lattice. A similar disorder was observed in the structures of hydrogen peroxide water solvates of PPh₄⁺ and AsPh₄⁺ halides (Churakov *et al.*, 2005). Hydrogen peroxide molecules are combined by strong O2—H2 \cdots O1 hydrogen bonds to give chains parallel to the *c* axis.

Both kinds of chains are organized in a three-dimensional network by peroxide–thymine O1—H1 \cdots O4 interactions (Fig. 4). Thus, the H₂O₂ molecule is involved in three hydrogen bonds with adjacent molecules, forming two donor and one acceptor interactions. The inclusion of the disordered water molecule does not break the packing motif while it forms three somewhat longer hydrogen bonds with the same neighbouring molecules.

Experimental

The crystals of the title compound were obtained by cooling down to –18° a saturated solution of thymine in 50% hydrogen peroxide. The experimental data were measured at 120 K due to the instability of the compound at ambient conditions.

Refinement

All hydrogen atoms were located in a difference Fourier map. The hydrogen peroxide H1 and H2 atoms were refined with the same U_{iso} and the H1—O1 and H2—O2 distances restrained to be approximately equal (SADI instruction in XL software). The water hydrogen atoms H3 and H4 were also refined with the same U_{iso} and the H3—O12 and H4—O12 distances restrained (SADI).

Figures

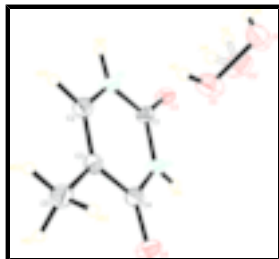


Fig. 1. The asymmetric unit of the title compound, showing the numbering scheme adopted. Displacement ellipsoids are shown at the 50% probability level.

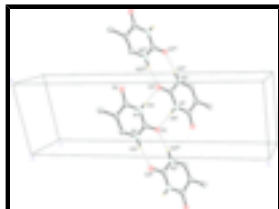


Fig. 2. The hydrogen bonded (dashed lines) chains of thymine molecules in the title compound parallel to the *ac* diagonal. H atoms not involved in hydrogen bonds are omitted. [Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $-x, 1 - y, 1 - z$; (iii) $1 + x, y, 1 + z$].

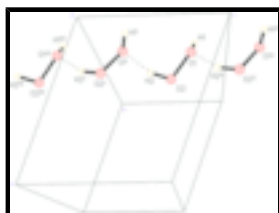


Fig. 3. The hydrogen bonded (dashed lines) chains of H_2O_2 molecules in the title compound parallel to the *c* axis. [Symmetry codes: (i) $x, 0.5 - y, -1/2 + z$; (ii) $x, 0.5 - y, 1/2 + z$; (iii) $x, y, -1 + z$].

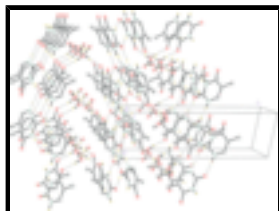


Fig. 4. The three-dimensional hydrogen bonded network (dashed lines) in the title compound. H atoms not involved in hydrogen bonds are omitted.

Thymine hydrogen peroxide 0.55-solvate 0.45-hydrate

Crystal data

$\text{C}_5\text{H}_6\text{N}_2\text{O}_2 \cdot 0.55\text{H}_2\text{O}_2 \cdot 0.45\text{H}_2\text{O}$

$M_r = 152.93$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 6.5047\ (16)\ \text{\AA}$

$b = 19.194\ (5)\ \text{\AA}$

$c = 5.6190\ (13)\ \text{\AA}$

$\beta = 110.078\ (5)^\circ$

$V = 658.9\ (3)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 321.6$

$D_x = 1.542\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1539 reflections

$\theta = 3.3\text{--}29.5^\circ$

$\mu = 0.13\ \text{mm}^{-1}$

$T = 120\ (2)\ \text{K}$

Prism, colourless

$0.20 \times 0.20 \times 0.10\ \text{mm}$

Data collection

Bruker SMART 1K diffractometer	1733 independent reflections
Radiation source: fine-focus sealed tube	1174 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.038$
$T = 120(2)$ K	$\theta_{\text{max}} = 29.0^\circ$
ω scans	$\theta_{\text{min}} = 2.1^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2003)	$h = -7 \rightarrow 8$
$T_{\text{min}} = 0.974$, $T_{\text{max}} = 0.987$	$k = -25 \rightarrow 23$
4556 measured reflections	$l = -6 \rightarrow 7$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.108$	$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
1733 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
147 parameters	$\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{\AA}^{-3}$
3 restraints	$\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.5189 (2)	0.43892 (7)	0.7551 (3)	0.0193 (3)	
N2	0.1954 (2)	0.43931 (7)	0.4159 (2)	0.0201 (3)	
O3	0.22793 (17)	0.50240 (5)	0.77214 (19)	0.0214 (3)	

supplementary materials

O4	0.81449 (18)	0.37725 (6)	0.7577 (2)	0.0269 (3)	
C1	0.3077 (2)	0.46216 (7)	0.6531 (3)	0.0180 (3)	
C2	0.2878 (3)	0.39447 (8)	0.2885 (3)	0.0206 (3)	
C3	0.4944 (2)	0.37063 (7)	0.3883 (3)	0.0187 (3)	
C4	0.6227 (2)	0.39384 (7)	0.6405 (3)	0.0192 (3)	
C5	0.5985 (3)	0.32256 (9)	0.2523 (3)	0.0239 (4)	
O1	0.0489 (5)	0.26290 (15)	0.7488 (6)	0.0323 (7)	0.55
O2	0.2145 (5)	0.29347 (15)	0.6611 (7)	0.0320 (7)	0.55
H1	-0.040 (7)	0.302 (2)	0.740 (9)	0.057 (11)*	0.55
H2	0.183 (8)	0.269 (2)	0.503 (8)	0.057 (11)*	0.55
O12	0.1421 (8)	0.2877 (2)	0.7417 (7)	0.0324 (8)	0.45
H3	0.041 (10)	0.320 (2)	0.711 (10)	0.049 (13)*	0.45
H4	0.124 (11)	0.269 (3)	0.592 (10)	0.049 (13)*	0.45
H22	0.191 (3)	0.3837 (9)	0.119 (3)	0.025 (5)*	
H53	0.501 (3)	0.3136 (9)	0.082 (4)	0.030 (5)*	
H52	0.638 (3)	0.2786 (10)	0.342 (4)	0.032 (5)*	
H11	0.590 (3)	0.4559 (10)	0.893 (4)	0.031 (5)*	
H51	0.738 (3)	0.3440 (10)	0.241 (3)	0.029 (5)*	
H21	0.055 (4)	0.4561 (11)	0.337 (4)	0.043 (6)*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0163 (6)	0.0200 (6)	0.0183 (7)	0.0007 (5)	0.0018 (5)	-0.0030 (5)
N2	0.0142 (6)	0.0223 (6)	0.0207 (7)	0.0020 (5)	0.0020 (5)	-0.0018 (5)
O3	0.0169 (6)	0.0230 (6)	0.0224 (6)	0.0026 (4)	0.0044 (5)	-0.0034 (4)
O4	0.0182 (6)	0.0316 (6)	0.0263 (6)	0.0081 (5)	0.0016 (5)	-0.0019 (5)
C1	0.0152 (7)	0.0163 (7)	0.0205 (8)	-0.0012 (5)	0.0036 (6)	0.0014 (6)
C2	0.0204 (8)	0.0218 (7)	0.0190 (8)	-0.0010 (6)	0.0059 (6)	-0.0007 (6)
C3	0.0205 (8)	0.0170 (7)	0.0196 (8)	-0.0012 (6)	0.0081 (6)	0.0001 (6)
C4	0.0188 (7)	0.0171 (7)	0.0223 (8)	0.0018 (6)	0.0079 (6)	0.0034 (6)
C5	0.0241 (8)	0.0241 (8)	0.0237 (9)	0.0028 (7)	0.0082 (7)	0.0000 (7)
O1	0.0287 (15)	0.0302 (15)	0.0441 (17)	0.0045 (12)	0.0201 (14)	0.0113 (12)
O2	0.0252 (15)	0.0292 (14)	0.0436 (19)	-0.0035 (11)	0.0143 (14)	0.0008 (12)
O12	0.026 (2)	0.037 (2)	0.032 (2)	0.0122 (18)	0.0064 (18)	-0.0006 (17)

Geometric parameters (\AA , $^\circ$)

N1—C1	1.3689 (19)	C3—C4	1.446 (2)
N1—C4	1.385 (2)	C3—C5	1.500 (2)
N1—H11	0.82 (2)	C5—H53	0.965 (19)
N2—C1	1.3544 (19)	C5—H52	0.972 (19)
N2—C2	1.382 (2)	C5—H51	1.016 (19)
N2—H21	0.93 (2)	O1—O2	1.453 (4)
O3—C1	1.2453 (18)	O1—H1	0.93 (4)
O4—C4	1.2361 (18)	O2—H2	0.97 (4)
C2—C3	1.346 (2)	O12—H3	0.87 (5)
C2—H22	0.968 (18)	O12—H4	0.89 (5)

C1—N1—C4	126.05 (14)	C4—C3—C5	118.65 (14)
C1—N1—H11	115.0 (14)	O4—C4—N1	118.51 (14)
C4—N1—H11	118.8 (14)	O4—C4—C3	125.46 (14)
C1—N2—C2	121.90 (13)	N1—C4—C3	116.03 (13)
C1—N2—H21	118.0 (13)	C3—C5—H53	111.0 (11)
C2—N2—H21	120.0 (13)	C3—C5—H52	110.7 (11)
O3—C1—N2	123.11 (13)	H53—C5—H52	109.1 (15)
O3—C1—N1	121.37 (14)	C3—C5—H51	110.4 (10)
N2—C1—N1	115.51 (14)	H53—C5—H51	107.8 (14)
C3—C2—N2	123.03 (15)	H52—C5—H51	107.7 (16)
C3—C2—H22	123.9 (10)	O2—O1—H1	100 (3)
N2—C2—H22	113.0 (10)	O1—O2—H2	99 (2)
C2—C3—C4	117.47 (14)	H3—O12—H4	105 (5)
C2—C3—C5	123.88 (14)		
C2—N2—C1—O3	-179.79 (14)	C1—N1—C4—O4	-179.59 (14)
C2—N2—C1—N1	1.2 (2)	C1—N1—C4—C3	1.0 (2)
C4—N1—C1—O3	179.41 (14)	C2—C3—C4—O4	-179.46 (15)
C4—N1—C1—N2	-1.5 (2)	C5—C3—C4—O4	-0.2 (2)
C1—N2—C2—C3	-0.4 (2)	C2—C3—C4—N1	-0.1 (2)
N2—C2—C3—C4	-0.1 (2)	C5—C3—C4—N1	179.10 (14)
N2—C2—C3—C5	-179.33 (14)	H1—O1—O2—H2	-113 (4)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O4 ⁱ	0.93 (4)	1.75 (4)	2.683 (3)	173 (5)
O12—H3 \cdots O4 ⁱ	0.87 (5)	1.93 (5)	2.764 (4)	160 (5)
O2—H2 \cdots O1 ⁱⁱ	0.97 (4)	1.52 (4)	2.446 (5)	159 (4)
O12—H4 \cdots O1 ⁱⁱ	0.89 (5)	1.92 (5)	2.798 (5)	172 (6)
N1—H11 \cdots O3 ⁱⁱⁱ	0.82 (2)	2.01 (2)	2.8347 (18)	178.1 (18)
N2—H21 \cdots O3 ^{iv}	0.93 (2)	1.90 (2)	2.8204 (18)	170.3 (18)

Symmetry codes: (i) $x-1, y, z$; (ii) $x, -y+1/2, z-1/2$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x, -y+1, -z+1$.

Fig. 1

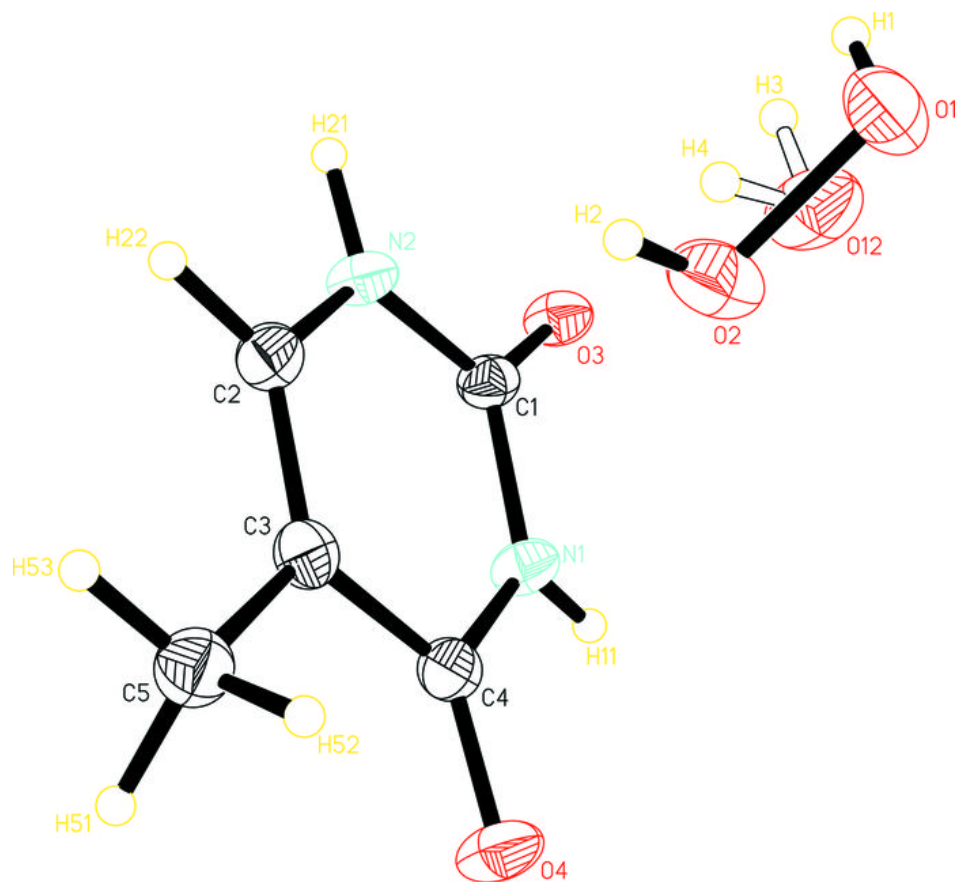


Fig. 2

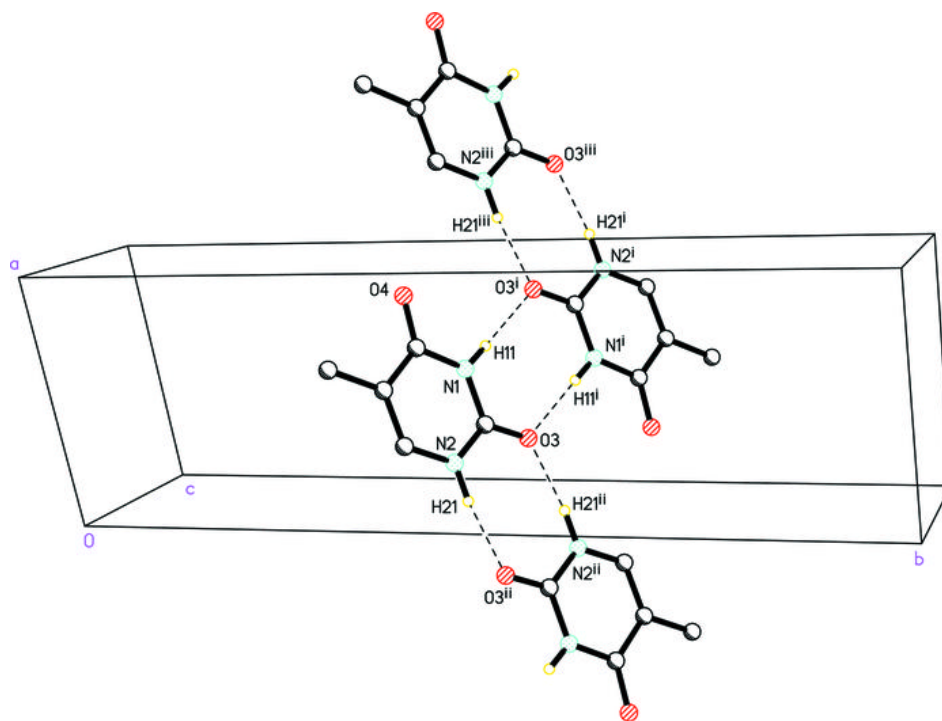


Fig. 3

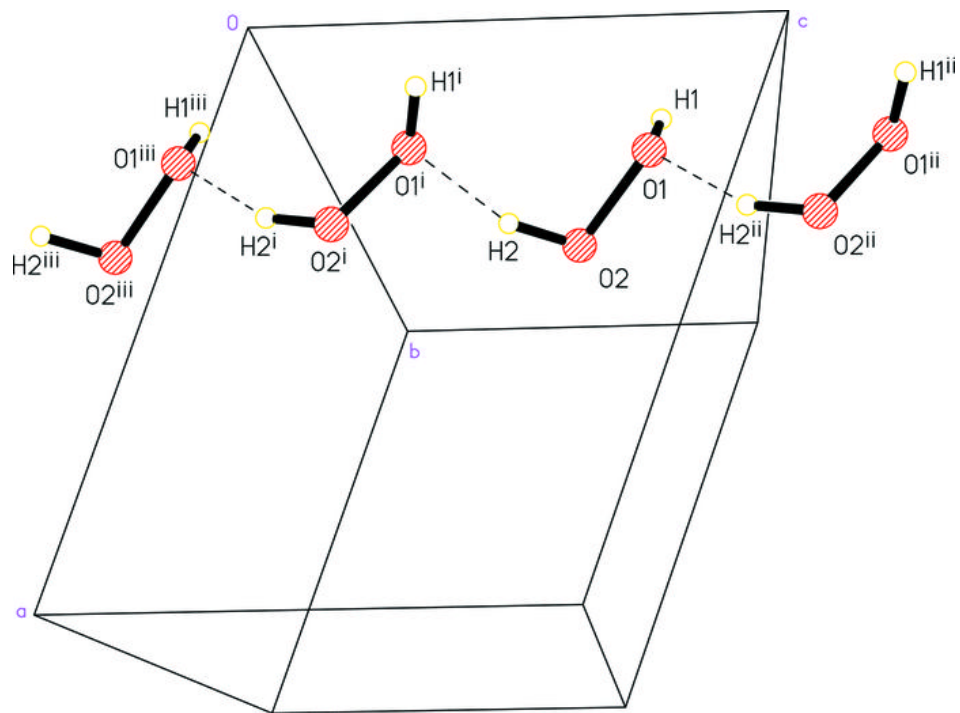


Fig. 4

