

## Structure of 5-Chloromercurio-2'-deoxyuridine

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**Abstract.** Chloro(2-deoxyuridin-5-yl)mercury, [HgCl(C<sub>9</sub>H<sub>11</sub>N<sub>2</sub>O<sub>5</sub>)],  $M_r = 463.24$ , monoclinic,  $P2_1$ ,  $a = 8.9319$  (6),  $b = 5.7057$  (6),  $c = 12.465$  (2) Å,  $\beta = 110.70$  (1)°,  $V = 594.3$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.589$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54184$  Å,  $\mu = 272.61$  cm<sup>-1</sup>,  $F(000) = 432.0$ ,  $T = 293$  K, final  $R = 0.034$  and  $wR = 0.047$  for 1091 observed reflections.

**Introduction.** 5-Chloromercurio-2'-deoxyuridine has been used extensively as a synthetic intermediate for the preparation of C5 substituted deoxyuridine derivatives *via* palladium-mediated reactions (Bergstrom, 1982; Bergstrom, Lin, Wang, Rotstein, Beal, Norrix & Ruth, 1992). C5-substituted deoxyuridine derivatives synthesized from 5-chloromercurio-2'-deoxyuridine include examples of potent antiviral agents (Cheng, Grill, Ruth & Bergstrom, 1980; Bergstrom, Ruth, Reddy & De Clercq, 1984) and compounds with linkage sites for bioconjugation to oligonucleotides (Goodchild, 1990). The insolubility of 5-chloromercurio-2'-deoxyuridine in either water or organic solvents has precluded certain identification of its structure. The crystallographic study outlined here now establishes that 5-chloromercurio-2'-deoxyuridine is monomeric and does have the expected structure.

**Experimental.** A colorless needle (dimensions 0.31 × 0.05 × 0.05 mm) obtained by slow evaporation from 0.1N NaCl solution was used for data collection on an Enraf-Nonius CAD-4 diffractometer, with graphite-monochromated Cu  $K\alpha$  radiation at 293 (1) K using the  $\omega$ - $2\theta$  scan technique ( $\omega$  varied from 1–16° min<sup>-1</sup>) to a  $2\theta$  maximum of 130.0°. A total of 1112 unique reflections were measured within the range  $-10 \leq h \leq 9$ ,  $0 \leq k \leq 6$ ,  $0 \leq l \leq 14$ , of which 1091 with  $I > 3\sigma(I)$  were used for all calculations. Three standard reflections monitored every 97 reflections showed no significant decrease in intensity indicating no crystal decay. Cell constants were refined with 25 reflections in the range  $45 < \theta < 47^\circ$ . Lorentz and polarization corrections were applied to the data. An empirical absorption correction based

on the method of Walker & Stuart (1983) was applied with minimum and maximum transmission factors of 0.3 and 1.0, respectively. The phase problem was solved using the Patterson heavy-atom method which revealed the position of the Hg atom [using *MolEN* (Fair, 1990)]. The remaining atoms were located in successive difference Fourier synthesis. H atoms were located and added to the structure-factor calculations but their positions were not refined. The structure was refined in full-matrix least squares where the function minimized was  $\sum w(|F_o| - |F_c|)^2$  and the weight  $w$  is defined according to the Killean & Lawrence (1969) method with terms of  $\text{PWT} = 0.020$  and  $\text{QWT} = 1.0$ ,  $w = 4F^2/\sigma(I)^2 + (PF^2)^2$ .

Atomic scattering factors and the values for  $\Delta f'$  and  $\Delta f''$  were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Anomalous-dispersion effects were included in  $F_c$  (Ibers & Hamilton, 1964). The final cycle of refinement included 162 variable parameters and converged with an unweighted agreement factor  $R$  ( $\sum ||F_o| - |F_c||/\sum F_o$ ) of 0.034, a weighted agreement factor  $wR$  of 0.047 and a  $(\Delta/\sigma)_{\text{max}}$  of 0.25.

The standard deviation of an observation of unit weight was 1.99. The final difference Fourier map showed no significant residual electron density and the highest peak had a maximum  $\rho$  of 3.14 e Å<sup>-3</sup> with an estimated error based on a  $\Delta F$  of 0.23 (Cruickshank, 1949). Plots of  $\sum w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $\sin\theta/\lambda$  and various classes of indices showed no unusual trends.

**Discussion.** Final positional parameters for the non-H atoms of 5-chloromercurio-2'-deoxyuridine are listed in Table 1.† An *ORTEP*II (Johnson, 1976) thermal ellipsoid drawing is given in Fig. 1, depicting

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71285 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR1008]

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Table 1. Table of positional parameters with their *e.s.d.*'s in parentheses

$B$  is defined as  $\exp\{-0.25[h^2a^*B(1,1) + k^2b^*B(2,2) + l^2c^*B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)]\}$  where  $a^*$ ,  $b^*$  and  $c^*$  are reciprocal lattice constants.

	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
Hg	0.59105 (4)	0.32830	0.37782 (3)	2.225 (9)
Cl	0.6599 (4)	0.6303 (8)	0.5082 (3)	3.65 (7)
O(2)	0.417 (1)	-0.448 (2)	0.0226 (8)	3.1 (2)
O(4)	0.257 (1)	0.163 (2)	0.1866 (8)	3.8 (2)
O(4')	0.8261 (9)	-0.501 (2)	0.2777 (7)	2.5 (2)
O(3')	0.9628 (9)	-0.649 (3)	0.0894 (7)	3.5 (2)
O(5')	1.073 (1)	-0.418 (3)	0.4879 (8)	5.0 (3)
N(1)	0.604 (1)	-0.272 (2)	0.1746 (8)	2.0 (2)
N(3)	0.3396 (8)	-0.158 (4)	0.1100 (7)	2.2 (2)
C(2)	0.450 (1)	-0.305 (2)	0.0950 (9)	1.9 (2)
C(4)	0.367 (1)	0.039 (3)	0.185 (1)	2.6 (3)
C(5)	0.530 (1)	0.062 (3)	0.259 (1)	2.6 (3)
C(6)	0.639 (1)	-0.085 (3)	0.250 (1)	2.3 (2)
C(1')	0.733 (1)	-0.414 (3)	0.1651 (9)	2.1 (2)
C(2')	0.851 (1)	-0.291 (3)	0.1252 (9)	2.3 (2)
C(3')	0.994 (1)	-0.461 (3)	0.167 (1)	2.1 (2)
C(4')	0.989 (1)	-0.535 (3)	0.2842 (9)	2.3 (3)
C(5')	1.091 (1)	-0.382 (5)	0.3796 (9)	3.9 (5)

Table 2. Table of bond distances (Å) and angles (°) with *e.s.d.*'s in parentheses

Hg—Cl	2.298 (4)	N(1)—C(1')	1.45 (2)
Hg—C(5)	2.06 (2)	N(3)—C(2)	1.35 (2)
O(2)—C(2)	1.18 (2)	N(3)—C(4)	1.43 (3)
O(4)—C(4)	1.22 (2)	C(4)—C(5)	1.43 (2)
O(4')—C(1')	1.44 (1)	C(5)—C(6)	1.31 (2)
O(4')—C(4')	1.44 (1)	C(1')—C(2')	1.49 (2)
O(3')—C(3')	1.40 (2)	C(2')—C(3')	1.54 (2)
O(5')—C(5')	1.43 (2)	C(3')—C(4')	1.54 (2)
N(1)—C(2)	1.39 (2)	C(4')—C(5')	1.49 (2)
N(1)—C(6)	1.39 (2)		
Cl—Hg—C(5)	179.0 (4)	C(4)—C(5)—C(6)	120 (1)
C(1')—O(4')—C(4')	109 (1)	N(1)—C(6)—C(5)	124 (1)
C(2)—N(1)—C(6)	121 (1)	O(4')—C(1')—N(1)	108 (1)
C(2)—N(1)—C(1')	119 (1)	O(4')—C(1')—C(2')	105 (1)
C(6)—N(1)—C(1')	119 (1)	N(1)—C(1')—C(2')	116 (1)
C(2)—N(3)—C(4)	128 (1)	C(1')—C(2')—C(3')	101 (1)
O(2)—C(2)—N(1)	123 (1)	O(4')—C(4')—C(5')	107 (1)
O(2)—C(2)—N(3)	123 (1)	C(3')—C(4')—C(5')	113 (1)
N(1)—C(2)—N(3)	114 (1)	O(3')—C(3')—C(4')	112 (1)
O(4)—C(4)—N(3)	121 (1)	O(3')—C(3')—C(2')	108 (1)
O(4)—C(4)—C(5)	126 (2)	C(4')—C(3')—C(2')	101 (1)
N(3)—C(4)—C(5)	113 (1)	O(4')—C(4')—C(3')	106 (1)
Hg—C(5)—C(4)	119 (1)	O(5')—C(5')—C(4')	115 (2)
Hg—C(5)—C(6)	121 (1)		

the numbering scheme. Bond lengths and angles are listed in Table 2.

The pyrimidine base is planar and the maximum deviation of a ring atom from the least-squares mean plane is 0.04 (1) Å. The Cl—Hg—C(5) bond angle is 179.0 (4)°, the C(5)—Hg bond length is 2.06 (2) Å and the Hg—Cl distance is 2.298 (4) Å. These values are in agreement with previously reported results for organomercury compounds (Atwood, Canada, Lau, Ludwick & Ludwick, 1978; Bach, Woodard, Anderson & Glick, 1982; Halfpenny & Small, 1979; Larock, Burns, Varapath, Russell, Richardson, Janakiraman & Jacobson, 1987).

The glycosidic torsion angle  $\chi$ , O(4')—C(1')—N(1)—C(2), is  $-134$  (1)°, which is within the usual range for pyrimidine nucleosides possessing the *anti* configuration (Saenger, 1984). The sugar pucker is C(2')-*endo*. The phase angle of pseudorotation and the amplitude of puckering (Altona & Sundaralingam, 1972) are  $P = 161.1^\circ$  and  $\tau_m = 42.3$ . The conformation of the C(5')—O(5') bond is *ap* and  $\gamma = 171$  (1)°. The conformational parameters are in accordance with the IUPAC—IUB Joint Commission on Biochemical Nomenclature (1983).

The packing diagram is presented in Fig. 2. Intermolecular hydrogen bonds are represented by dashed lines. Intermolecular heteroatom distances between O(3')...O(4), N(3)...O(3') and O(5')...O(5') are 2.70 (2), 2.95 (2) and 3.19 (2) Å, respectively. The same hydrogen-bonding network has been observed previously (Young, Tollin & Wilson, 1969).

The preparation of 5-chloromercurio-2'-deoxyuridine, an important intermediate in the synthesis of C5-substituted pyrimidine nucleoside derivatives, has been described by Bergstrom & Ruth (1977).

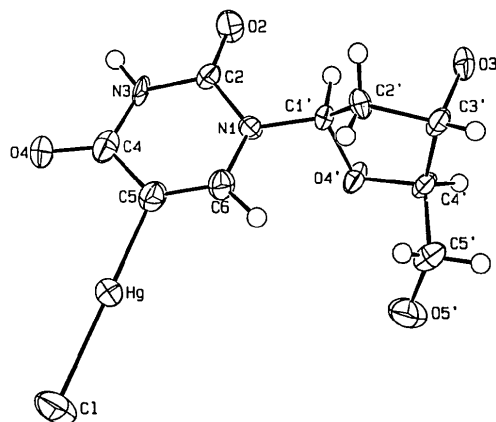


Fig. 1. ORTEP plot of the X-ray structure of 5-chloromercurio-2'-deoxyuridine.

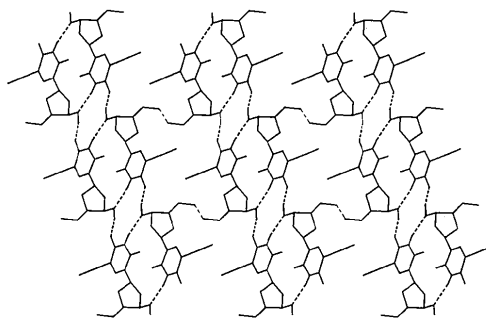


Fig. 2. Packing diagram for 5-chloromercurio-2'-deoxyuridine.

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## Structure of 1,2-Bis(spiro[2.3]hex-4-ene-4-yl)ethane

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**Abstract.**  $C_{14}H_{18}$  (1),  $M_r = 186.3$ , monoclinic,  $P2_1/c$ ,  $a = 9.285$  (6),  $b = 5.373$  (2),  $c = 11.981$  (6) Å,  $\beta = 112.09$  (4)°,  $V = 553.8$  (1) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.12$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 0.6$  cm<sup>-1</sup>,  $F(000) = 204$ ,  $T = 183$  K,  $R = 0.050$ ,  $wR = 0.049$  for 871 observed reflections. The molecule occupies a special position at an inversion centre. The bond lengths in the three-membered ring are undisturbed due to the opposing influence of the double-bond  $\pi$ -system conjugation with the Walsh molecular orbital of cyclopropane and strain due to a spiro conjunction of two small rings.

**Introduction.** Continuing our structural investigation of the new class of hydrocarbons, triangulanes (Zefirov, Kozhushkov, Kuznetsova, Kokoreva,

Lukin, Ugrak & Tratch, 1990) and their derivatives, we report in the present paper the results of an X-ray study of (1). The compound was obtained by the reaction of the linear triangulane 1,1-dibromotri-spiro[2.0.2.1]heptane with MeLi. The details of synthesis, chemistry and spectra of (1) will be published elsewhere. Besides the unequivocal confirmation of the structure of (1), the present study seemed of interest because there were no structural data on compounds with spiro-conjugated cyclopropane (CP) and cyclobutane rings (according to the Cambridge Crystallographic Database, Release 1991).

**Experimental.** A single transparent colourless crystal with approximate dimensions  $0.2 \times 0.25 \times 0.4$  mm was mounted on a Siemens P3/PC four-circle diffractometer (graphite-monochromated, Mo  $K\alpha$  radia-

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