Discussion. The positional coordinates are given in Table 1.* Fig. 1 shows a projection of the molecule with the atomic numbering. Bond lengths and angles are given in Table 2.

The molecule of the title compound contains an *N*-methylpyridinium moiety joined to a 4*H*-imidazole which has a pentamethylene group substituted at the spiranic C(1) atom.

The pyridine ring is planar (average torsion angle 0·8°) and the five-membered ring is near planar (average torsion angle 2·59°). N(2)–C(3) [1·281 (6) Å] is a localized double bond in the five-membered ring. The identity of the bond distances N(4)–C(5) [1·313 (6)] and C(5)–N(17) [1·315 (8) Å], shorter than the value usually found for a single C—N bond, reflects the conjugation of this amidine portion of the molecule (Takayanagi, Ogura, Matsuzaki, Kitajima & Nishimura, 1979).

In particular, the short C(3)–C(12) bond and the small torsion angle about this bond may be attributed to the conjugation between the imidazole and pyridinium groups. This is in good agreement with the previously studied compound 5′-amino-2′-(2-pyridyl)cyclohexanespiro-4′-4′*H*-imidazole (Avendaño, Ramos, Bellanato, Smith-Verdier, Florencio & García-Blanco, 1984).

The cyclohexane ring adopts a slightly flattened chair conformation with approximate mirror symmetry [C_s plane through C(1) and C(8), with $C_s^1 = 1\cdot30$ (1), $C_2^{7-8} = 3\cdot39$ (2) and $C_2^{6-7} = 8\cdot64$ (2) (Duax & Norton, 1975)]. The deviations of C(1) and C(8) from the plane through the remaining atoms of the ring are −0·633 (5) and 0·679 (7) Å, respectively; consequently the C(6), C(1), C(10) part of the ring is a little more flattened than the opposite C(7), C(8), C(9) part.

The molecules in the crystal are held together by van der Waals contacts and are also connected by N—H···N hydrogen bonds [N(17)···N(4)($-x+\frac{1}{2}, -y+\frac{1}{2}, -z-\frac{1}{2}$) 3·043 (7), H(17)···N(4) = 2·36 (8) Å, angle N(17)–H(17)···N(4) 175·°].

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39859 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a 1/1 Complex of 3′,5′-Di-*O*-acetyl-5-bromo-2′-deoxyuridine and 3′,5′-Di-*O*-acetyl-5-iodo-2′-deoxyuridine, $C_{13}H_{15}Br_{0.5}I_{0.5}N_2O_7$

By C. C. Wilson and P. Tollin

Carnegie Laboratory of Physics, University of Dundee, Dundee DD1 4HN, Scotland

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Abstract. $M_r = 414\cdot7$, $P2_12_12_1$, $a = 7\cdot708$ (3), $b = 26\cdot835$ (5), $c = 7\cdot805$ (3) Å, $U = 1614\cdot42$ Å^3, $Z = 4$, $D_x = 1\cdot71$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 21\cdot82$ cm^{-1}, $F(000) = 828$, $T = 293$ K, $R = 0\cdot062$ for 2400 reflections (Friedel pairs not merged). The glycosidic torsion angle, χ, is −133·3 (11)°, and the sugar pucker is $^2T_1$ [C(1′)-*exo*, C(2′)-*endo*] with $P = 137\cdot2$ (14)°. The conformation about C(4′)–C(5′) is *gauche–gauche* (g^+). There is one hydrogen bond, N(3)···O(3′1) [2·914 (18) Å]. Close contacts are present between halogen and O(5′1) [average 3·21 (2) Å] and between acetyl O(5′1) and a neighbouring base ring, 2·93 (3) Å. The halogen position is occupied randomly by Br and I atoms.

Introduction. A previously determined structure in our series of substituted nucleosides, 3′,5′-di-*O*-acetylthymidine (AT) (Wilson, Low, Tollin & Wilson,

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1984), showed that in its hydrogen-bonded base-paired dimer one of the molecules adopted the conformation of 3′,5′-di-*O*-acetyl-5-iodo-2′-deoxyuridine (AIDU) (Wilson, Low & Young, 1983), the other that of the bromo-substituted version (ABDU) (Low, 1983). Consequently we attempted to co-crystallize these two acetyl-substituted compounds in order to ascertain whether or not such a complex would base-pair in the same fashion as AT.

Experimental. Crystals were grown from a 1/1 mixture of ABDU and AIDU in aqueous-ethanol solution. Cell dimensions were measured on a Stoe Stadi II two-circle diffractometer from a crystal mounted along **a**. Intensity data collected from crystals mounted along **a** (dimensions 1·81 × 0·59 × 0·27 mm) and along **c** (dimensions 1·78 × 0·58 × 0·17 mm); *a*-axis crystal in the range $h = 0$ to 6, *c*-axis crystal in the range $l = 0$ to 4. Max. $\sin\theta/\lambda$ 0·77 Å^{-1}; $\pm h$, $\pm k$, $\pm l$. Absorption corrections applied: *a*-axis crystal had max. and min. transmission factors of 0·58 and 0·27, *c*-axis crystal 0·39 and 0·02. Standard reflection measured every 100 reflections; random intensity variation <5% from mean intensity. Total of 11 320 reflections measured, 3542 with $I < 4\sigma(I)$ regarded as unobserved; two sets of reflection data merged, 2400 reflections used in the solution; index range $h \pm 9$, k 0/30, l 0/10; $R_{\rm int} = 6{\cdot}7\%$. Structure solved by heavy-atom method. Refinement by blocked-matrix least squares, with *SHELX*76 (Sheldrick, 1976). All atoms except H refined using anisotropic temperature factors; H/atoms included as riding atoms at calculated positio~~ns~~, with $U_{\rm iso}$ fixed at 1·5 times that of the parent atom. Final refinement involved 217 refined parameters, $R \doteq 0{\cdot}062$, $wR = 0{\cdot}087$, $w = 2{\cdot}4018/[\sigma^2(F) + 0{\cdot}003691F^2]$; max. $\Delta/\sigma = 0{\cdot}066$; max. difference-map peak 2·85 e Å^{-3}, min. −2·26 e Å^{-3}; the highest difference peaks were associated with the halogen position. Scattering factors from *International Tables for X-ray Crystallography* (1974). Other computer programs used: *XANADU* (Roberts & Sheldrick, 1975), *PLUTO* (Motherwell & Clegg, 1978); calculations carried out on the Dundee University DEC-10 computer.

The halogen position

The unit cell was almost exactly twice the size of that of the monoclinic AIDU, the cell being doubled in one of the dimensions, but was confirmed as being orthorhombic with one formula unit in the asymmetric unit, by intensity measurements. That both Br and I are present was confirmed by energy dispersive X-ray microanalysis (EDX). In $P2_12_12_1$ with $Z = 4$ the halogen positions must necessarily be randomly occupied by Br and I. Refinement was carried out in several ways to check this supposition. The refinement which produced the best combination of low residual and sensible temperature factors, quoted here, was obtained by constraining the C(5)—halogen distances close to those of AIDU and ABDU, with each halogen atom given a site occupancy of 0·5. Refinements attempted using an averaged scattering factor for the halogen (Pd^{2+}) (Klug, 1947), using only Br or only I in the 5-position, and using unconstrained refinement with Br, I occupancies of 0·5, were all less satisfactory.

Discussion. Atomic coordinates are given in Table 1,* bond lengths, bond angles and selected torsion angles in Table 2. The atomic numbering used is shown in the perspective drawing (Fig. 1). The molecule is very similar in most respects to that of AIDU, with the C(5)—halogen distances, at 1·925 (10) [C(5)—Br] and 2·034 (8) Å [C(5)—I], constrained close to their values in ABDU (1·884 Å) and AIDU (2·046 Å). Bond distances and angles are similar to those in AIDU, to within the limits of error.

Molecular conformations

Torsion angles agree well with values in AIDU; the molecule is *anti* about the glycosidic bond, χ[C(2)—N(1)—C(1′)—O(4′)] = −133·3 (11)°, with sugar-ring pucker $^2T_1$ [C(1′)-*exo*, C(2′)-*endo*] [$P = 137{\cdot}2$ (14)°, $\psi_m = 34{\cdot}4$ (14)°]. The C(4′)—C(5′) conformation of the sugar is *gauche–gauche* (g^+), φ_1[O(4′)—C(4′)—C(5′)—O(5′)] = −65·7 (11)°, and φ_2[C(3′)—C(4′)—C(5′)—O(5′)] = 52·9 (11)°. These agree well with the situation in AIDU, where the sugar pucker is E_1 [C(1′)-*exo*, $P = 132{\cdot}0°$] and the C(4′)—C(5′) conformation angle φ_1 −56·9°. These conformational details are normal for pyrimidine nucleosides. The pyrimidine ring is planar to within 0·015 (3) Å [N(1)], and the acetyl groups are also planar, to within 0·006 (3) Å [C(3′1)] and 0·009 (3) Å [C(5′1)], for the 3′ and 5′ groups respectively.

Hydrogen bonding and molecular stacking

The complex does not, as was hoped, form base-paired dimers, instead generally following the stacking scheme observed in AIDU; close contacts are listed in Table 3. As in AIDU, there is one hydrogen bond present: N(3)···O(3′1)($1+x,y,z-1$), with N···O 2·914 (18), and H···O 1·87 Å. The close halogen–halogen contacts [shortest I···Br = 4·224 (15) Å] have been noted previously (Rahman & Wilson, 1970), as have the close halogen–O contacts [I···O(5′1) 3·152 (21), Br···O(5′1) 3·263 (21) Å] (Camerman & Trotter, 1965). However, the carbonyl O involved here, O(5′1), is unusual in that the previously noted such halogen–O contacts, including that in AIDU, were with

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39908 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Coordinates* ($\times 10^4$) *for non-hydrogen atoms and equivalent isotropic temperature factors* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Br	1851 (10)	−7222 (3)	−4303 (13)	74 (1)
I	1910 (4)	−7251 (1)	−4217 (6)	40 (1)
N(1)	−1394 (9)	−5991 (3)	−5167 (8)	42 (1)
C(2)	−790 (14)	−5760 (3)	−6640 (10)	47 (2)
O(2)	−1469 (9)	−5394 (2)	−7237 (8)	58 (1)
N(3)	671 (8)	−5982 (3)	−7348 (8)	39 (1)
C(4)	1549 (12)	−6407 (3)	−6798 (10)	45 (2)
O(4)	2827 (9)	−6561 (3)	−7559 (9)	62 (2)
C(5)	813 (10)	−6629 (3)	−5242 (10)	39 (2)
C(6)	−621 (12)	−6418 (3)	−4513 (10)	43 (2)
C(1′)	−2949 (11)	−5796 (3)	−4324 (10)	44 (2)
C(2′)	−4497 (11)	−6130 (4)	−4475 (11)	50 (2)
C(3′)	−5522 (11)	−6009 (3)	−2813 (10)	42 (2)
O(3′)	−6701 (8)	−5607 (2)	−3275 (7)	44 (1)
C(3′1)	−7853 (11)	−5482 (3)	−2031 (11)	45 (2)
O(3′1)	−7920 (9)	−5704 (3)	−678 (9)	69 (2)
C(3′2)	−9030 (13)	−5060 (4)	−2495 (13)	65 (2)
C(4′)	−4137 (12)	−5819 (3)	−1549 (10)	41 (2)
C(5′)	−3763 (13)	−6152 (3)	−47 (10)	46 (2)
O(5′)	−3370 (9)	−6639 (2)	−739 (8)	58 (1)
C(5′1)	−2577 (15)	−6958 (4)	331 (14)	60 (2)
O(5′1)	−2211 (14)	−6849 (3)	1773 (11)	90 (2)
C(5′2)	−2195 (21)	−7448 (5)	−566 (15)	88 (3)
O(4′)	−2525 (7)	−5769 (2)	−2532 (7)	44 (1)

Table 2. *Interatomic distances* (Å) *and angles* (°), *and selected torsion angles* (°)

C(5)–Br	1·925 (10)	O(4′)–C(1′)	1·438 (10)
C(5)–I	2·034 (8)	C(3′)–C(2′)	1·553 (12)
C(2)–N(1)	1·387 (10)	O(3′)–C(3′)	1·458 (10)
C(6)–N(1)	1·389 (11)	C(4′)–C(3′)	1·540 (12)
C(1′)–N(1)	1·464 (11)	C(3′1)–O(3′)	1·357 (10)
O(2)–C(2)	1·207 (11)	O(3′1)–C(3′1)	1·213 (11)
N(3)–C(2)	1·389 (12)	C(3′2)–C(3′1)	1·496 (14)
C(4)–N(3)	1·394 (11)	C(5′)–C(4′)	1·502 (11)
O(4)–C(4)	1·223 (11)	O(4′)–C(4′)	1·466 (10)
C(5)–C(4)	1·467 (11)	O(5′)–C(5′)	1·445 (10)
C(6)–C(5)	1·366 (11)	C(5′1)–O(5′)	1·343 (12)
C(2′)–C(1′)	1·496 (12)	O(5′1)–C(5′1)	1·197 (14)
		C(5′2)–C(5′1)	1·519 (16)
C(6)–N(1)–C(2)	122·0 (7)	O(4′)–C(1′)–C(2′)	106·7 (6)
C(1′)–N(1)–C(2)	119·1 (7)	C(3′)–C(2′)–C(1′)	102·5 (7)
C(1′)–N(1)–C(6)	118·8 (7)	O(3′)–C(3′)–C(2′)	105·3 (6)
O(2)–C(2)–N(1)	122·6 (9)	C(4′)–C(3′)–C(2′)	104·5 (7)
N(3)–C(2)–N(1)	114·2 (7)	C(4′)–C(3′)–O(3′)	110·2 (6)
N(3)–C(2)–O(2)	123·2 (8)	C(3′1)–O(3′)–C(3′)	114·4 (6)
C(4)–N(3)–C(2)	128·5 (7)	O(3′1)–C(3′1)–O(3′)	122·0 (8)
O(4)–C(4)–N(3)	121·2 (8)	C(3′2)–C(3′1)–O(3′)	114·2 (7)
C(5)–C(4)–N(3)	113·6 (7)	C(3′2)–C(3′1)–O(3′1)	123·8 (8)
C(5)–C(4)–O(4)	125·2 (8)	C(5′)–C(4′)–C(3′)	115·9 (7)
C(4)–C(5)–Br	119·4 (6)	O(4′)–C(4′)–C(3′)	106·4 (6)
C(4)–C(5)–I	119·9 (6)	O(4′)–C(4′)–C(5′)	107·5 (7)
C(6)–C(5)–Br	121·3 (6)	O(5′)–C(5′)–C(4′)	106·6 (6)
C(6)–C(5)–I	120·8 (6)	C(5′1)–O(5′)–C(5′)	116·0 (7)
C(6)–C(5)–C(4)	119·3 (7)	O(5′1)–C(5′1)–O(5′)	122·4 (9)
C(5)–C(6)–N(1)	122·4 (7)	C(5′2)–C(5′1)–O(5′)	110·7 (9)
C(2′)–C(1′)–N(1)	113·8 (7)	C(5′2)–C(5′1)–O(5′1)	126·8 (10)
O(4′)–C(1′)–N(1)	105·6 (6)	C(4′)–O(4′)–C(1′)	108·2 (6)

C(2)–N(1)–C(1′)–O(4′)	−133·3 (11)
O(4′)–C(1′)–C(2′)–C(3′)	34·6 (11)
C(2′)–C(1′)–O(4′)–C(4′)	−31·1 (9)
C(1′)–C(2′)–C(3′)–C(4′)	−25·2 (11)
C(2′)–C(3′)–C(4′)–O(4′)	7·7 (11)
C(3′)–C(4′)–O(4′)–C(1′)	13·8 (9)
O(4′)–C(4′)–C(5′)–O(5′)	−65·7 (11)
C(3′)–C(4′)–C(5′)–O(5′)	52·9 (11)

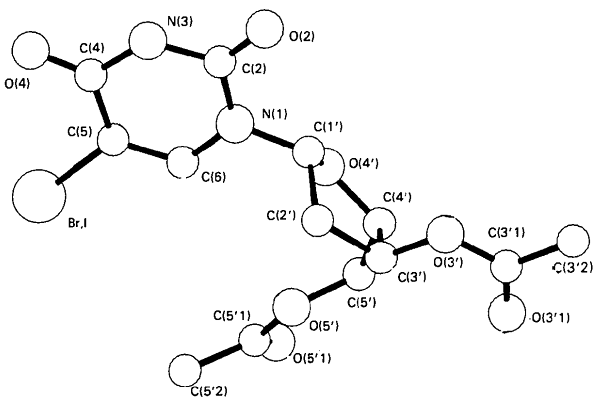

Fig. 1. Perspective view of the molecule showing the atomic numbering. Halogen position averaged.

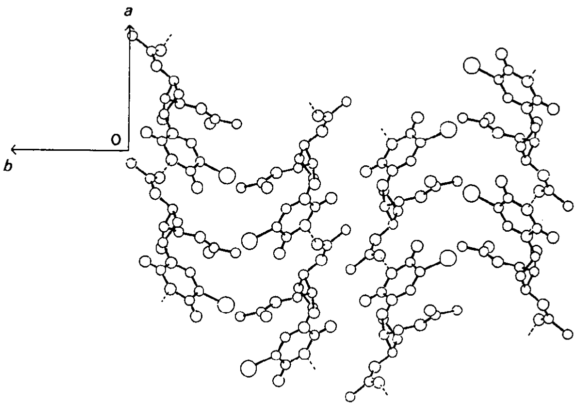

Fig. 2. View along **c**, showing the molecular stacking. Other axes as shown. Halogen position shown as an average.

Table 3. *Close contacts* (Å) *of interest*

O(3′1)(1+x,y,z−1)···N(3)	2·914 (18)	I···I	4·259 (12)
···H(3)	1·871 (18)	I···Br	4·224 (15)
		Br···Br	4·273 (15)
O(5′1)(x,y,z−1)···N(1)	3·377 (21)	I···O(5′1)	3·152 (21)
···C(2)	3·358 (21)	Br···O(5′1)	3·263 (21)
···N(3)	3·290 (21)		
···C(4)	3·324 (21)		
···C(5)	3·348 (21)		
···C(6)	3·353 (21)		

exocyclic O atoms attached to the base ring, whereas here the interaction is with an acetyl O. The presence of the flexible acetyl groups interrupts the usual nucleoside intermolecular interactions, by donating carbonyl O which are employed in preference to those O atoms directly connected to the pyrimidine ring. This preference is exhibited in both hydrogen bonds and other interatomic interactions, in the present case including the halogen···O contact noted above, and the stacking interaction described below. A C=O carbonyl dipole, O(5′1) at (*x,y,z*−1), points down on the pyrimidine base ring, the distance of O(5′1) from the ring plane being 2·93 (3) Å; the distances from the ring atoms are given in Table 3. The distances involved in this contact here indicate that the interaction is not quite as pronounced as in AIDU, the O atom in this case being 0·1 Å further from the ring. This interaction has now appeared in four of our recent structures, the three others being AIDU, AT, and 2′,3′,5′-tri-*O*-acetyluridine (Low & Wilson, 1984), and plainly plays an important stacking role in the absence of base–base stacking interactions. The molecules stack as shown in Fig. 2.

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Absolute Configuration of (−)-*cis*-2-Ethylcyclohexanamine Hydrochloride 0·39-Ethanol Solvate, $C_8H_{18}N^+.Cl^-.0{\cdot}39C_2H_6O$

BY GERD KNUPP AND AUGUST W. FRAHM*

Institut für Pharmazeutische Chemie der Universität Bonn, Kreuzbergweg 26, D-5300 Bonn 1, Federal Republic of Germany

AND ARMIN KIRFEL, TILL FRÖHLICH AND GEORG WILL

Lehrstuhl für Mineralogie und Kristallographie, Mineralogisches Institut der Universität Bonn, Poppelsdorfer Schloss, D-5300 Bonn 1, Federal Republic of Germany

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Abstract. $M_r = 181{\cdot}7$, orthorhombic, *I*222, $a = 10{\cdot}804\ (4)$, $b = 13{\cdot}173\ (4)$, $c = 15{\cdot}275\ (4)$ Å, $Z = 8$, $V = 2174$ Å^3, $D_m = 1{\cdot}08$, $D_x = 1{\cdot}110$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}02$ cm^{-1}, $F(000) = 801{\cdot}12$, $T = 293$ K, final $R = 0{\cdot}031$ for 1866 observed reflections. Under enantiomeric and diastereomeric control 2-substituted cyclohexanones are converted by reductive amination and hydrogenolysis to *cis*-2-substituted cyclohexanamine hydrochlorides. The absolute configuration of one of these products, (−)-*cis*-2-ethylcyclohexanamine hydrochloride, could be elucidated as 1*R*,2*S*, which corroborates the results of circular-dichroism studies on the corresponding *N*-salicylidene derivates of the primary amines.

Introduction. Recently we have reported an efficient synthesis of optically active *cis*-2-substituted cyclohexanamines of types (1) and (2) with high enantiomeric purity (Knupp & Frahm, 1981, 1984). The absolute configurations of these compounds were predicted from circular-dichroism (CD) studies of the corresponding *N*-salicylidene derivatives (3) of the primary amines (2) (Knupp & Frahm, 1984) and by comparison with the known absolute configuration of the enantiomeric *cis*-2-phenylcyclohexanamine (Verbit & Price, 1972). In view of known CD behaviour, particularly of cyclic amines, which is due to conformational change (Ripperger, Schreiber, Snatzke & Ponsold, 1969) additional proof is now given by X-ray structure analysis of the title compound, (−)-(2*b*).HCl (4), the details of which are reported here.

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* To whom correspondence should be addressed.

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