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The Molecular and Crystal Structure of the Sodium Salt of Deoxyadenosine-5'-phosphate Hexahydrate

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The crystal structure of the sodium salt of deoxyadenosine-5'-phosphate hexahydrate has been determined by X-ray diffraction techniques. The unit cell is orthorhombic, space group $P2_12_12_1$, with cell dimensions $a = 43.64$ (2), $b = 6.908$ (4), $c = 6.826$ (4) Å and $Z = 4$. The data (1806 reflexions) were collected photographically by equi-inclination Weissenberg geometry and estimated visually. The structure was solved by the symbolic addition procedure and refined to an R value of 0.060. 24 out of 25 hydrogen atoms were located. The sugar ring has the conformation $C(2')$ -endo, $C(3')$ -endo and the glycosidic torsional angle (χ_{C-N}) is 63.4° . The sugar ring oxygen $O(1')$ seems to participate in a hydrogen bond with the amino nitrogen of the base, a feature hitherto not clearly shown in similar structures. The stacking of adenine bases at 3.45 Å with considerable overlap is another interesting feature. The sodium ion has a nearly octahedral coordination with water oxygen atoms at distances of 2.374 to 2.454 Å. The crystal structure may be viewed as consisting of alternate channels of water molecules (sodium ion polyhedra) and nucleotides.

Introduction

Recently, Jacob and colleagues at our Institute have prepared many nucleic acid reactive antibodies for immunological studies, specific to deoxyribonucleotide antigens and in particular to deoxyadenosine-5'-monophosphate (5'-dAMP) (Humayun & Jacob, 1973). This paper reports the complete molecular and crystal structure of this nucleotide.* The present analysis continues our earlier studies on the conformations of DNA constituents (Viswamitra, Reddy, Lin & Sundaralingam, 1971).

Experimental

Crystal growth and crystal data

The material used in the present work was obtained from Sigma Chemical Company (U.S.A.) as a disodium salt of 2'-deoxyadenosine-5'-monophosphoric acid. It

was crystallized by slow diffusion of dioxane into water solutions of the sample. The crystal data were obtained from rotation, Weissenberg and precession photographs using $Cu K\alpha$ radiation (Table 1). The density measured by the flotation method using a mixture of carbon tetrachloride and acetone is 1.53 g cm^{-3} , suggesting a chemical formula of the molecule in the asymmetric unit as $C_{10}H_{13}N_5Na_2O_6P \cdot 5H_2O$ ($d_{\text{calc}} = 1.511 \text{ g cm}^{-3}$). However, detailed structure analysis showed that the molecule exists as $C_{10}H_{13}N_5NaO_6P \cdot 6H_2O$, in the crystal. The crystal data are presented in Table 1 and the numbering scheme for the molecule is shown in Fig. 1.

Intensity data

The intensity data were collected with $Cu K\alpha$ radiation from a crystal of size $0.5 \times 0.4 \times 0.25$ mm, by the equi-inclination Weissenberg technique for layers $hk0$ – $hk6$ and $h0l$. In all, 1806 reflexions were estimated visually by using a calibrated film strip prepared with the experimental crystal. The data were corrected for

* A preliminary communication on this structure has already appeared (Reddy & Viswamitra, 1973).

Table 1. *Crystal data for the sodium salt of deoxyadenosine-5'-phosphate hexahydrate*

Formula	$C_{10}H_{13}N_5O_6P \cdot Na \cdot 6H_2O$
M.W.	461.3
System	Orthorhombic
<i>a</i>	43.640 (20) Å
<i>b</i>	6.908 (4)
<i>c</i>	6.826 (4)
<i>V</i>	2057.8 Å ³
<i>Z</i>	4
<i>d</i> _{meas}	1.53 g cm ⁻³
<i>d</i> _{calc}	1.511 g cm ⁻³
μ (Cu <i>K</i> α)	21.06 cm ⁻¹
Systematic absences	<i>h</i> 00: <i>h</i> odd 0 <i>k</i> 0: <i>k</i> odd 00 <i>l</i> : <i>l</i> odd
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁

Lorentz-polarization factors and scaled to absolute values by a Wilson plot. Absorption corrections were not applied ($\mu_r=0.42$).

Structure determination and refinement

The position of the phosphorous atom ($x=0.335$, $y=0.0$, $z=0.70$) was located from Harker sections of a sharpened Patterson map. The minimum function maps based on the phosphorus position were rather ambiguous because of spurious symmetry caused by the special disposition of the molecule in the crystal structure (see the section below on molecular packing).

Following the symbolic addition procedure for non-centrosymmetric crystals (Karle & Karle, 1966) about 75 phases were generated by hand computation. The origin and enantiomorph reflexions were selected as specified by Hauptman & Karle (1956) (Table 2). The initial set of phases was refined and extended to 350 by the use of the tangent refinement formula (Karle & Hauptman, 1956) with *E* greater than 1.2. An *E* map was computed from 275 reflexions with highest *E* values.

Table 2. *Origin specification*

<i>E</i>	<i>h</i>	<i>k</i>	<i>l</i>	ϕ	
3.62	15	0	5	$\pi/2$	} Origin assignment
2.53	31	1	0	$\pi/2$	
3.37	0	7	2	$\pi/2$	
2.91	14	0	5	$\pi/2$	} Enantiomorph assignment
3.24	36	5	2	$a=\pi/2$	
3.05	17	2	2	$b=0$	} from symbolic addition
				$a=137.3^\circ$	} Final values at the end of refinement.
				$b=7.8$	

Hardly any peaks in the asymmetric unit were seen in sections other than $y=0.0$ and $y=0.25$. It was not possible to locate the complete molecule. Seven strong peaks in the *E* map were chosen for the structure-factor calculation; six peaks were taken as oxygens and one as phosphorus (the position of phosphorus was the same as that found earlier from the Patterson map). Successive structure-factor and Fourier computations gave a structure in which one could clearly identify a complete chemically feasible nucleotide, one sodium atom and six water oxygens.

This structure, however, did not refine below an *R* value 0.26. Careful model building was employed to locate the correct set of atomic sites, with the original structure at $R=0.26$ retained as far as possible. This exercise led to a new structure with 18 atoms at the same positions as in the original structure; the remaining 11 atoms changed their coordinates y to $-y$. The new structure also needed a renumbering of many original peaks.

Four cycles of isotropic refinement of this structure using a block-diagonal least-squares program reduced the *R* value to 0.107, and it further reduced to 0.074 after four cycles of anisotropic refinement. A difference synthesis computed at this stage showed clearly 22 out of 25 hydrogen atoms available in the asymmetric unit, with peak heights varying from 0.4 to 0.7 e Å⁻³. With these hydrogens included in the refinement the *R* index converged to a final value 0.060.* Two more hydrogen atoms were located from a final difference synthesis (peak height 0.3 to 0.4 e Å⁻³, $\sigma(\rho)=0.1$ e Å⁻³). The function minimized in the re-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30593 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

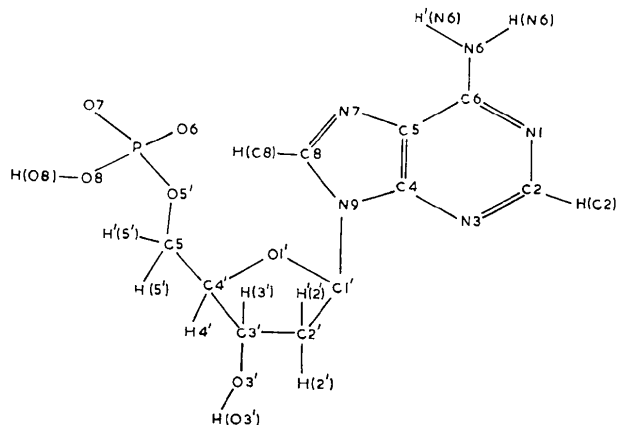


Fig. 1. Atomic numbering in deoxyadenosine-5'-phosphate.

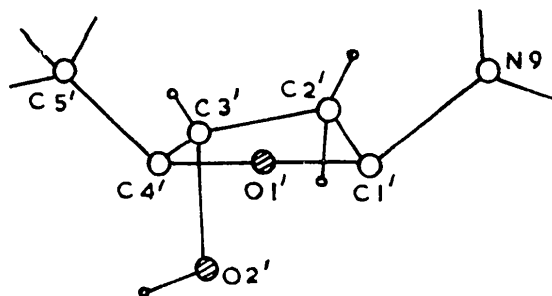


Fig. 2. A view of the deoxyribose moiety showing the puckering of C(2') and C(3') with respect to the C(1')-O(1')-C(4') plane.

Table 3. *Positional and thermal parameters*

(a) Positional parameters of the non-hydrogen atoms
All parameters and their standard deviations given in parentheses have been multiplied by 10^5 .

	<i>x</i>	<i>y</i>	<i>z</i>
P	33494 (3)	-1075 (27)	69816 (24)
O(6)	30616 (9)	-557 (87)	57700 (67)
O(7)	33633 (11)	11999 (82)	87439 (75)
O(8)	34104 (11)	-22956 (85)	75427 (91)
O(5')	36414 (10)	4554 (72)	56639 (74)
C(5')	37005 (14)	-6736 (105)	39160 (115)
C(1')	43546 (13)	22624 (108)	35243 (96)
C(2')	40794 (16)	36559 (114)	34236 (115)
C(3')	38409 (12)	25714 (118)	22655 (96)
O(3')	38586 (10)	30385 (87)	2201 (76)
C(4')	39175 (13)	4015 (103)	26097 (97)
O(1')	42190 (9)	3599 (70)	34875 (68)
N(1)	54315 (11)	25790 (102)	66675 (84)
C(2)	53357 (14)	26247 (147)	47607 (111)
N(3)	50561 (12)	25603 (113)	40725 (80)
C(4)	48459 (13)	24741 (110)	55101 (98)
C(5)	49063 (12)	24378 (95)	74914 (89)
C(6)	52152 (14)	25241 (101)	81103 (98)
N(6)	53027 (12)	25379 (112)	99633 (82)
N(7)	46352 (11)	23778 (98)	85926 (86)
C(8)	44210 (13)	23436 (122)	72436 (98)
N(9)	45301 (11)	24092 (100)	53369 (78)
Na	24881 (6)	50344 (53)	39297 (39)
W(1)	24486 (10)	74140 (76)	13885 (78)
W(2)	24323 (10)	26493 (79)	14402 (77)
W(3)	29347 (10)	1551 (89)	17794 (76)
W(4)	19335 (12)	52600 (96)	44636 (90)
W(5)	30452 (14)	50852 (135)	35914 (114)
W(6)	39483 (12)	66620 (102)	-14134 (124)

finement was $\sum w(|F_o| - |F_c|)^2$, the weighting function employed being

$$w = 1/(a + b|F_o| + c|F_c|)^2$$

where $a = 12.0$, $b = 1.0$, $c = 0.00476$. For hydrogen atoms the scattering factors of Stewart, Davidson & Simpson (1965) were used. For other atoms scattering factors were computed using a function developed by Cromer & Waber (1965).

Results

The final heavy-atom positions and thermal parameters are listed in Table 3, and those of the hydrogen atoms in Table 4. The bond distances and angles involving non-hydrogen atoms are given in Table 5. The average bond distances involving hydrogen atoms are C-H = 0.99, O-H = 0.90, N-H = 0.91 Å. The average estimated standard deviations in various bond lengths are $\sigma(\text{P-O}) = 0.006$, $\sigma(\text{C, N, O-C}) = 0.01$ and $\sigma(\text{C, N, O-H}) = 0.1$ Å, and the average standard deviations in bond angles involving non-hydrogen atoms vary from 0.3 to 0.6°.

Molecular conformation and geometry

Glycosidic bond

The torsion angle χ describing the relative orientation of the base and sugar about the glycosidic bond

Table 3 (cont.)

(b) Anisotropic thermal parameters of the non-hydrogen atoms

All parameters and their standard deviations given in parentheses have been multiplied by 10^5 . The temperature factor is of the form: $\exp[-(b_{11}h^2 + \dots + 2b_{12}hk + \dots)]$.

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
P	13 (1)	1186 (33)	886 (35)	-21 (5)	0 (4)	226 (33)
O(6)	20 (2)	2143 (128)	1239 (115)	19 (15)	-31 (11)	166 (120)
O(7)	31 (2)	2316 (139)	1172 (123)	-42 (17)	21 (14)	-77 (108)
O(8)	33 (2)	1643 (127)	2894 (170)	-23 (15)	31 (16)	845 (128)
O(5')	26 (2)	1471 (118)	1464 (120)	-56 (13)	44 (12)	-199 (94)
C(5')	22 (3)	1200 (144)	1576 (180)	-26 (17)	15 (18)	-70 (128)
C(1')	21 (3)	1676 (160)	783 (156)	36 (18)	-45 (15)	143 (133)
C(2')	40 (4)	1503 (163)	1290 (196)	-2 (21)	-87 (21)	311 (147)
C(3')	21 (3)	1817 (168)	793 (151)	15 (19)	4 (15)	215 (142)
O(3')	23 (2)	2574 (164)	1301 (123)	-57 (15)	-42 (13)	489 (113)
C(4')	21 (3)	1414 (169)	933 (149)	6 (16)	-17 (15)	-109 (118)
O(1')	15 (2)	1695 (121)	1372 (114)	10 (12)	-31 (11)	-230 (97)
N(1)	21 (2)	2144 (153)	906 (134)	1 (17)	-21 (13)	-228 (135)
C(2)	19 (3)	2820 (236)	1226 (176)	-56 (23)	25 (17)	-176 (181)
N(3)	29 (3)	2869 (191)	528 (125)	2 (21)	-14 (14)	219 (139)
C(4)	23 (3)	1365 (158)	1055 (160)	31 (19)	-3 (16)	139 (143)
C(5)	25 (3)	869 (129)	911 (151)	36 (18)	-34 (16)	-235 (119)
C(6)	29 (3)	1048 (138)	892 (148)	-39 (18)	7 (16)	81 (135)
N(6)	28 (3)	2363 (170)	592 (129)	-35 (19)	-20 (13)	106 (130)
N(7)	24 (2)	1768 (148)	1139 (139)	-30 (16)	1 (14)	-47 (131)
C(8)	22 (3)	2087 (189)	771 (153)	-34 (20)	-4 (15)	-59 (150)
N(9)	22 (2)	1931 (146)	519 (119)	-2 (16)	-7 (12)	-40 (121)
Na	37 (1)	1260 (52)	1145 (58)	-11 (8)	-9 (7)	-27 (58)
W(1)	36 (2)	1191 (107)	1963 (137)	18 (14)	-29 (14)	-37 (113)
W(2)	33 (2)	1414 (113)	1794 (134)	-14 (14)	-12 (14)	-65 (113)
W(3)	32 (2)	2354 (143)	1466 (126)	-38 (17)	-12 (13)	98 (130)
W(4)	42 (3)	2311 (161)	2161 (147)	-28 (18)	-58 (16)	-688 (138)
W(5)	53 (4)	4471 (261)	3065 (202)	12 (28)	108 (21)	-495 (253)
W(6)	34 (3)	2576 (180)	4732 (256)	19 (18)	-79 (23)	1494 (192)

Table 4. *Positional parameters of the hydrogen atoms*

Positional parameters and their standard deviations in parentheses have been multiplied by 10^3 .

	x	y	z	B
H(O8)	362 (2)	-245 (12)	-746 (12)	4.9 (1.8)
H(C5')	380 (2)	-183 (11)	434 (11)	2.7 (1.7)
H'(C5')	348 (2)	-34 (15)	304 (15)	5.7 (2.5)
H(C4')	391 (2)	-6 (11)	131 (11)	2.2 (1.6)
H(O3')	370 (2)	238 (13)	-20 (13)	3.1 (1.8)
H(C3')	363 (2)	310 (15)	271 (15)	5.1 (2.5)
H(C2')	405 (2)	368 (17)	457 (17)	6.4 (2.8)
H'(C2')	411 (2)	475 (18)	281 (18)	7.3 (2.9)
H(C1')	449 (1)	230 (10)	202 (10)	1.5 (1.3)
H(C8)	422 (2)	183 (11)	738 (11)	1.9 (1.5)
H(N6)	519 (2)	221 (16)	1087 (15)	4.9 (2.5)
H'(N6)	550 (2)	319 (12)	1034 (12)	2.9 (1.7)
H(C2)	548 (2)	247 (17)	358 (17)	5.7 (2.8)
H(W1)	270 (2)	198 (15)	636 (15)	4.8 (2.3)
H'(W1)	241 (3)	141 (20)	708 (22)	9.4 (3.5)
H(W2)	230 (2)	205 (14)	98 (13)	3.3 (2.1)
H'(W2)	260 (1)	188 (8)	150 (8)	0.0 (1.0)
H(W3)	304 (1)	27 (10)	306 (10)	1.3 (1.3)
H'(W3)	308 (2)	94 (15)	94 (14)	5.0 (2.4)
H(W4)	312 (2)	581 (18)	-123 (17)	7.5 (3.1)
H(W5)	312	531	219	5.0
H'(W5)	327	500	406	5.0
H(W6)	394 (2)	591 (12)	-41 (11)	2.5 (1.6)
H'(W6)	582 (2)	206 (17)	639 (17)	6.9 (3.0)

is 63.4° . Therefore, the conformation is *anti* (for definition of the angles see Sundaralingam, 1969). This corresponds to the normal range preferred by most of the purine nucleotides, but differs appreciably from that found in AMP(3') ($\chi_{CN} = 3.9^\circ$, Sundaralingam, 1966) and AMP(5') ($\chi_{CN} = 22^\circ$, Kraut & Jensen, 1963). It is close to the χ value (69°) found in ATP(5') (Kenward *et al.*, 1971).

The best four-atom plane for deoxyribose (Table 6, plane II) is defined by C(1')-O(1')-C(4')-C(3'). C(2') is displaced from this plane by 0.450 \AA , lying on the same side as C(5') (Fig. 2). Hence the conformation of the deoxyribose ring is C(2')-*endo*. When referred to the three-atom plane C(4')-O(1')-C(1'), the conformation may be described as C(2')-*endo*, C(3')-*endo* (Table 6, plane III, Fig. 2). Table 7 lists the puckering of sugar in 12 deoxyribo compounds collected from the literature.

The torsion angles about the bonds of the sugar ring and those involving hydrogen atoms are given in Table 8.

The C(4')-C(5') bond

The conformation about the bond C(4')-C(5') is *gauche-gauche*, a normal conformation observed in the 5'-nucleotides, the exceptions being deoxyguanosine-5'-phosphate (Seshadri & Viswamitra, 1974) and 6-azauridine-5'-phosphate (Saenger & Suck, 1973) where *gauche-trans* conformation was observed. The angles O(1')-C(4')-C(5')-O(5') and C(3')-C(4')-C(5')-O(5') are -72.1 and 47.0° respectively.

The phosphate

The phosphate group is in characteristic staggered

conformation about the C(5')-O(5') bond. The torsion angles are C(5')-O(5')-P-O(6) 56.5° ; C(5')-O(5')-P-O(7) 175.7° , C(5')-O(5')-P-O(8) -58.0° . The ester linkage C(5')-O(5') shows the elongated conformation as usual; the torsion angle C(4')-C(5')-O(5')-P is 163.4° . The bond distances agree with those in similar monoionic phosphate groups. All oxygens except O(5') in the ester linkage participate in hydrogen-bond formation.

Table 5. *Bond distances (\AA) and angles ($^\circ$) involving non-hydrogen atoms*

P—O(6)	1.504 (4)	O(8)—P—O(5')	103.5 (3)
P—O(7)	1.506 (6)	P—O(5')-C(5')	118.1 (4)
P—O(8)	1.582 (6)	O(5')-C(5')-C(4')	109.6 (6)
P—O(5')	1.608 (5)	O(1')-C(1')-N(9)	107.1 (5)
O(5')-C(5')	1.449 (9)	O(1')-C(1')-C(2')	104.4 (5)
C(5')-C(4')	1.498 (10)	N(9)-C(1')-C(2')	113.8 (6)
C(4')-C(3')	1.554 (11)	C(3')-C(2')-C(1')	104.6 (6)
C(4')-O(1')	1.446 (7)	O(3')-C(3')-C(2')	111.2 (6)
O(1')-C(1')	1.442 (9)	O(3')-C(3')-C(4')	110.6 (5)
C(1')-C(2')	1.541 (10)	C(2')-C(3')-C(4')	104.6 (5)
C(2')-C(3')	1.507 (10)	O(1')-C(4')-C(5')	108.6 (5)
C(3')-O(3')	1.435 (9)	O(1')-C(4')-C(3')	106.1 (5)
C(1')-N(9)	1.459 (8)	C(5')-C(4')-C(3')	115.6 (6)
N(1)-C(6)	1.365 (8)	C(1')-O(1')-C(4')	111.3 (5)
N(1)-C(2)	1.367 (9)	C(6)-N(1)-C(2)	118.4 (6)
C(2)-N(3)	1.308 (8)	N(1)-C(2)-N(3)	128.8 (7)
N(3)-C(4)	1.345 (8)	C(2)-N(3)-C(4)	112.1 (6)
C(4)-C(5)	1.378 (9)	N(3)-C(4)-C(5)	125.9 (6)
C(5)-C(6)	1.414 (8)	N(3)-C(4)-N(9)	128.2 (6)
C(6)-N(6)	1.321 (9)	C(5)-C(4)-N(9)	105.9 (6)
N(7)-C(5)	1.402 (8)	C(4)-C(5)-N(7)	111.4 (6)
C(8)-N(7)	1.312 (8)	C(4)-C(5)-C(6)	118.4 (6)
N(9)-C(8)	1.387 (8)	N(7)-C(5)-C(6)	130.2 (6)
N(9)-C(4)	1.384 (7)	N(6)-C(6)-N(1)	119.4 (6)
		N(6)-C(6)-C(5)	124.2 (6)
O(6)-P-O(7)	117.3 (3)	N(1)-C(6)-C(5)	116.4 (6)
O(6)-P-O(8)	107.3 (3)	C(8)-N(7)-C(5)	103.0 (6)
O(6)-P-O(5')	110.4 (3)	N(7)-C(8)-N(9)	114.4 (6)
O(7)-P-O(8)	111.9 (3)	C(4)-N(9)-C(8)	105.2 (6)
O(7)-P-O(5')	105.7 (3)	C(4)-N(9)-C(1')	126.7 (6)
		C(8)-N(9)-C(1')	127.8 (6)

Table 6. *Least-squares planes through the base and sugar*

Equations of the planes

Plane I	$-0.0387X + 0.9991Y + 0.0172Z = 0.9572$
Plane II	$-0.0375X + 0.9990Y + 0.0235Z = 1.0066$
Plane III	$0.3691X - 0.0984Y - 0.9242Z = 4.6090$
Plane IV	$0.4076X - 0.1652Y - 0.8982Z = 5.3270$

Atom	Plane I	Plane II	Atom	Plane III	Plane IV
N(1)	-0.017	-0.011	C(1')	0.028	0.000
C(2)	0.010	0.008	C(2')	-0.450*	-0.590*
N(3)	0.007	0.000	C(3')	-0.025	-0.175*
C(4)	-0.003	-0.004	C(4')	0.032	0.000
C(5)	-0.014	0.007	O(1')	-0.036	0.000
C(6)	0.002	0.103	C(5')	-1.064*	-1.060*
N(7)	0.003	0.013*			
C(8)	-0.008	-0.004*			
N(9)	0.004	0.000*			
N(6)	0.016	0.036*			
C(1')	-0.086*	0.099*			
r.m.s. Δ	0.010	0.008		0.031	0.000
σ (i.m.s.)	0.006	0.007		0.006	0.006

* Atoms not included in the calculation of the plane.

Table 7. *Compounds with deoxyribose moiety*

Compound	Abbreviation	Puckering	$\chi(\text{C-N})$	Reference
1 Deoxyadenosine	DA	C(3')- <i>exo</i> [C(3')- <i>exo</i> , C(2')- <i>endo</i>]	10.9° <i>anti</i>	Watson, Sutor & Tollin (1965)
2 Thymidine	T	C(3')- <i>exo</i> [C(3')- <i>exo</i> , C(2')- <i>endo</i>]	39.0 <i>anti</i>	Young, Tollin & Wilson (1969)
3 Dihydrothymidine	DHT	O(1')- <i>endo</i>	72.0 <i>anti</i>	Konnert, Karle & Karle (1970)
4 5-Iodo-2'-deoxyuridine	IUDR	C(2')- <i>endo</i>	63.3 <i>anti</i>	Camerman & Trotter (1965)
5 5-Bromo-2'-deoxyuridine and 5-bromouridine	BUDR BUR	C(2')- <i>endo</i>	47.2 <i>anti</i>	Iball, Morgan & Wilson (1966)
6 Deoxyguanosine-5-bromo-deoxycytidine complex	DG:DC	C(2')- <i>endo</i> C(2')- <i>endo</i>	DG: 211 <i>syn</i> DC: 61 <i>anti</i>	Haschemeyer & Sobell (1965)
7 Deoxycytidine hydrochloride	DC.HCl	C(3')- <i>endo</i> [C(3')- <i>endo</i> , C(2')- <i>exo</i>]	0 <i>anti</i>	Subramanian & Hunt (1970)
8 Deoxycytidine-5'-phosphate monohydrate	5'-dCMP	C(3')- <i>exo</i>	-6.1 <i>anti</i>	Viswamitra, Reddy, Lin & Sundaralingam (1971)
9 Deoxyadenosine-5'-phosphate hexahydrate (sodium salt)	5'-dAMP. Na	C(2')- <i>endo</i> [C(2')- <i>endo</i> , C(3')- <i>endo</i>]	63.4 <i>anti</i>	Present work
10 Thymidine-5'-phosphate, calcium salt	5'-TMP. Ca	C(3')- <i>endo</i> [C(3')- <i>endo</i> , C(2')- <i>endo</i>]	48.0 <i>anti</i>	Trueblood, Horn & Luzzati (1961)
11 5-Fluoro-2'-deoxyuridine	FDU	C(2')- <i>endo</i>	59.0 <i>anti</i>	Harris & MacIntyne (1964)
12 Sodium-3',5'-thymidyl-5'-thymidylate	Na _p T _p T	C(2')- <i>endo</i> [C(2')- <i>endo</i> , C(3')- <i>exo</i>]		Camerman & Fawcett (1973)

Table 8. *Torsion angles (°) in the deoxyribose moiety of 5'-dAMP*Conformation of deoxyribose: C(2')-*endo*, C(3')-*endo*.

(a) Involving ring atoms

C(4')-O(1')-C(1')-C(2')	-23.2
O(1')-C(1')-C(2')-C(3')	-30.4
C(1')-C(2')-C(3')-C(4')	26.3
C(2')-C(3')-C(4')-O(1')	12.9
C(3')-C(4')-O(1')-C(1')	6.9

(b) Involving ring hydrogen atoms

H(1')-H(2')	14.5
H(1')-H(2')	38.7
H(2')-H(3')	-51.4
H'(2')-H(3')	76.8
H(3')-H(4')	-73.4

Molecular packing and hydrogen bonding

Figs. 3 and 4 show the molecular packing and hydrogen bonding viewed down the *b* and *c* axes. The special nature of the atomic disposition at $y=0.0$ and 0.25 is seen in Fig. 4. A brief discussion of the molecular packing is given below.

Base stacking

An interesting feature of the crystal structure is the stacking of the adenine bases (related by a 2_1 screw along the *b* axis) on top of each other at intervals of 3.45 Å (Figs. 5 and 6). Parallel stacking of bases is a major stabilizing force in a great number of crystal structures. Bugg (1972) and Bugg, Thomas & Sundaralingam (1971) have reviewed the various solid-state base-stacking patterns. In the present structure, the overlap is such that N(7), C(5), C(4), C(6), N(1) and N(6) of one ring lie practically on top of N(1),

C(6), N(6), C(5), N(7) and C(4) respectively of the neighbouring molecule. The bases are perpendicular to the *b* axis (the normal to the base plane is only 3.5° away from the *b* axis).

Partial overlap of adenine bases has been observed previously in other adenine derivatives. The bases are stacked at intervals of 3.86 Å in deoxyadenosine (Watson, Sutor & Tollin, 1965), 3.26 Å in 8,5-anhydro-2',3'-isopropylidene-8-mercaptoadenine (Tomita, Nishida, Fujiwara & Ikehara, 1970), 3.40 Å in adenosine-5-bromouridine (Haschemeyer & Sobell, 1965), 3.276 Å in 1-methylthymine and 9-methyladenosine (Hoogsteen, 1963), 3.30 Å in α -D-2'-amino-2'-deoxyadenosine (Rohrer & Sundaralingam, 1970) and 3.40 Å in adenosine-5'-triphosphate (Kennard *et al.*, 1971). A comparative study of base stacking in three deoxyribonucleotides is presented in Fig. 5.

Examination of residual electron density between the bases

In view of the nature of the base stacking it was felt worth while to examine the residual electron densities between the bases. The final difference map at $R=0.06$ is shown (near the base region only) in Fig. 6. It is seen that midway between the two rings there is a concentration of electron density up to a maximum of 0.4 e Å⁻³ ($\sigma(\rho)=0.1$ e Å⁻³). These densities therefore appear to be significant and suggest a considerable overlap of the electron distributions of the neighbouring rings.

It must be mentioned that the final $\Delta\rho(xyz)$ map does not show any significant residual electron density along the bonds of the base (in general less than 0.1 e Å⁻³). $\Delta\rho(xyz)$ along the bonds of the deoxyribose moiety, however, shows peak heights of up to 0.3 e Å⁻³.

Hydrogen bonding

All the available hydrogen atoms participate in hydrogen bonding. The bond lengths and angles of observed hydrogen bonds are listed in Table 9.

One of the amino hydrogen atoms belonging to N(6) points towards O(1') ($1-x, y-\frac{1}{2}, \frac{3}{2}-z$) [$O(1') \cdots H-N(6) = 154^\circ$]. The O(1')-N(6) distance is 3.1 Å, which is smaller by 0.5 Å than the total van der Waals distance for O, H, and N atoms (van der Waals radii: H=1.2, N=1.5, O=1.4 Å, Pauling, 1960). We therefore suggest that this is a weak hydrogen bond. Such a hydrogen bond has not been reported so far in other nucleotide structures. Nearest contact distances of 2.95 to 3.3 Å from O(1') have been observed by many workers. These, however, are normal van der Waals contacts and cannot be attributed to hydrogen-bond formation as there is no hydrogen atom in the neighbourhood. The only previous mention of a possible hydrogen bond from O(1') is that of a bifurcated hydrogen bond connecting a water molecule in α -D-2'-amino-2'-deoxyadenosine (Rohrer & Sundaralingam, 1970). The hydrogen bonding between phosphate oxy-

gens and other groups of the nucleotide is shown in Figs. 3 and 4).

The amino nitrogen N(6) hydrogen bonds with N(3) ($x, y, z+1$), and W(6) forms a hydrogen bond with N(1) ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$). These hydrogen bonds are nearly in the plane of the base and are probably among the factors responsible for the bases stacking in parallel sheets along the (010) plane.

In all the previous structures containing adenine, it has been found that N(7) of the base participates either in hydrogen-bond formation or in metal coordination. For example, N(7) is seen hydrogen bonded in 3'-AMP (Sundaralingam, 1966), dA (Watson, Sutor & Tollin, 1965), 1-methylthymine and 9-methyladenosine (Hoogsteen, 1963) *etc.*, and participating in metal coordination in 9-methylhypoxanthine (with Cu; Sletten, 1971), the zinc adenine-zinc guanine complex (with Zn; Srinivasan & Taylor, 1970), and adenosine triphosphate (with Na; Kennard *et al.*, 1971) *etc.*

However, in the present structure N(7) participates neither in hydrogen bonding nor in sodium coordination. The close stacking of adenine bases as mentioned

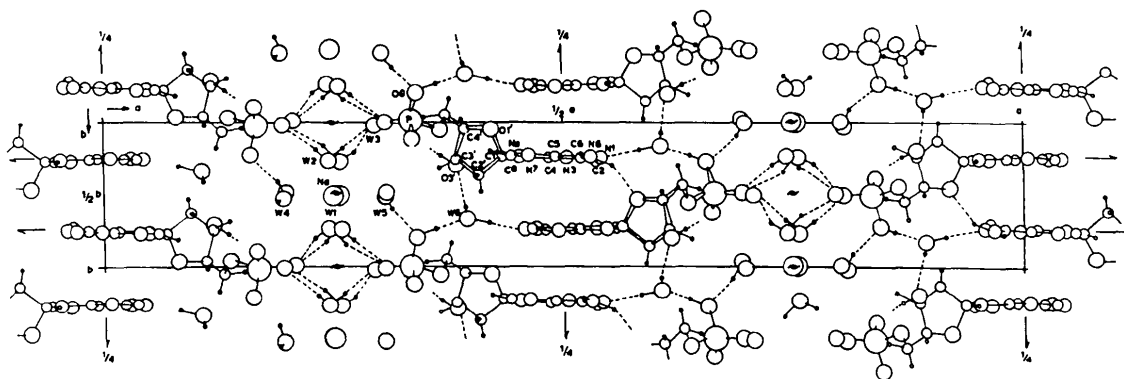


Fig. 3. Intermolecular hydrogen-bonding scheme and packing viewed along the b axis. Some of the hydrogen bonds are not indicated, for the sake of clarity. The stacking of the bases (perpendicular to base plane) and the sodium coordination polyhedra are shown.

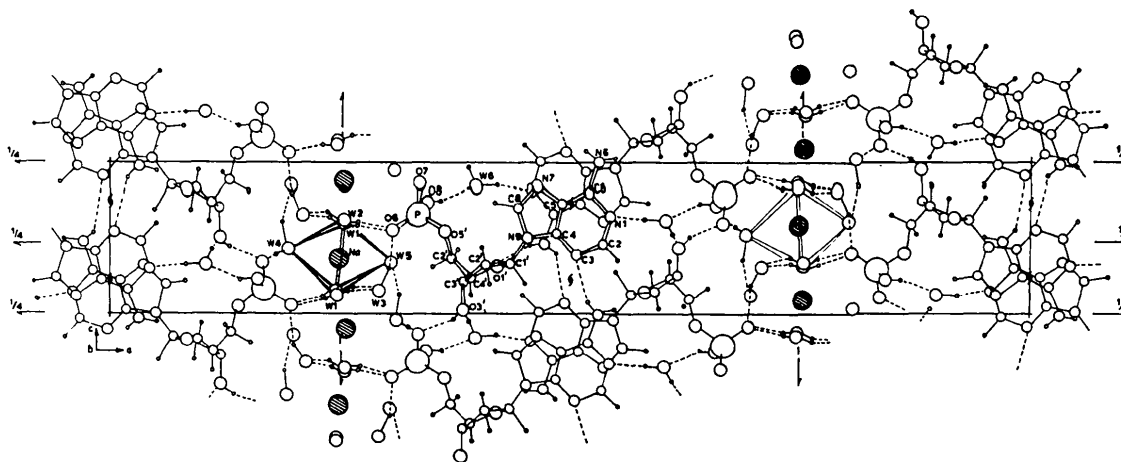


Fig. 4. Intermolecular hydrogen-bonding scheme and packing viewed along the c axis. The stacking viewed along the base is shown.

above with N(7) overlapping N(1) of the neighbouring molecule, might perhaps prevent additional coordination of hydrogen bonding for steric reasons.

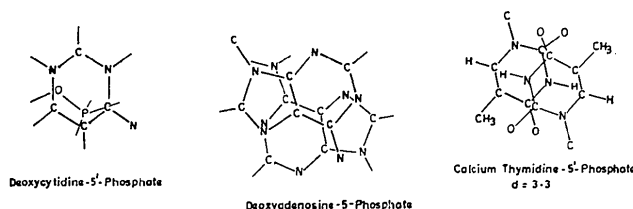


Fig. 5. Base-stacking patterns in deoxyribonucleotides.

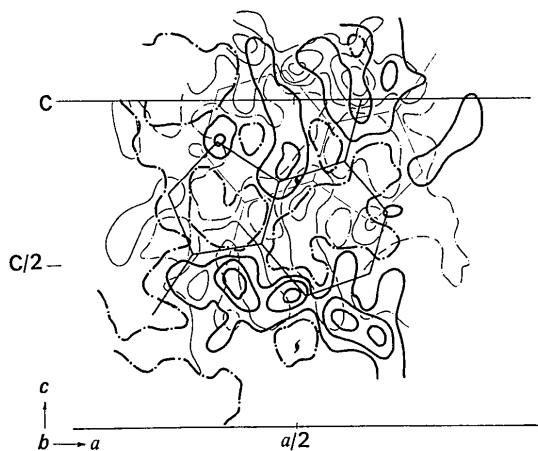


Fig. 6. Sections of a residual electron-density map projected on the (010) plane. The contours start at $0.1 \text{ e } \text{Å}^{-3}$ and are drawn at intervals of $0.1 \text{ e } \text{Å}^{-3}$. The sections shown are at $y=0.5$ and 0.0 (drawn as thick and thin contours respectively). The bases at $y=0.75$ and 0.25 (related by a 2_1 screw along the b axis) are also shown by thick and thin lines respectively. These electron densities appear to be significant and suggest a considerable overlap of the electron distributions of the neighbouring rings.

Sodium coordination

The sodium ion is surrounded by six water oxygens $W(1)$, $W(2)$, $W(4)$, $W(5)$, $W(1)$ ($\frac{1}{2}-x, -y, \frac{1}{2}+z$), $W(2)$ ($\frac{1}{2}-x, -y, \frac{1}{2}+z$), describing a nearly octahedral environment at distances 2.374 to 2.454 Å (Table 10). No other nucleotide structure seems to have such a regular metal coordination. The neighbouring octahedra share edges defined by $W(1)$ and $W(2)$ and form a channel of sodium and water molecules along the screw axis parallel to the c axis. This type of packing of alternate channels of nucleotides and water/metal molecules seems to be characteristic of many nucleotide structures (Viswamitra, Reddy, James & Williams, 1972).

Table 10. Sodium coordination polyhedra

Symmetry code		$i \quad \frac{1}{2}-x, 1-y, \frac{1}{2}+z$	
Na- $W(2)^i$	2.370 (6) Å	$W(2)^i$ -Na- $W(4)$	89.7 (0.2)°
Na- $W(2)$	2.379 (6)	$W(2)$ -Na- $W(1)$	87.2 (0.2)
Na- $W(1)$	2.396 (6)	$W(2)$ -Na- $W(1)^i$	91.3 (0.2)
Na- $W(1)^i$	2.399 (6)	$W(2)$ -Na- $W(5)$	92.5 (0.2)
Na- $W(5)$	2.443 (6)	$W(2)$ -Na- $W(4)$	92.8 (0.2)
Na- $W(4)$	2.453 (6)	$W(1)$ -Na- $W(1)^i$	177.0 (0.2)
Na-Na ⁱ	3.415 (4)	$W(1)$ -Na- $W(5)$	89.6 (0.2)
		$W(1)$ -Na- $W(4)$	89.6 (0.2)
		$W(1)^i$ -Na- $W(5)$	87.8 (0.2)
		$W(1)^i$ -Na- $W(4)$	93.1 (0.2)
		$W(5)$ -Na- $W(4)$	174.5 (0.3)
		$W(2)^i$ -Na- $W(2)$	177.2 (0.2)°
		$W(2)^i$ -Na- $W(1)$	94.1 (0.2)
		$W(2)^i$ -Na- $W(1)^i$	87.3 (0.2)
		$W(2)^i$ -Na- $W(5)$	85.0 (0.2)

All the computations were carried out on an IBM 360/44 computer with the programs written by Reddy (1973).

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Table 9. Hydrogen bonds and angles

Symmetry codes					
i	$x, y-1, z+1$	ii	$x, y, z-1$	iii	$x, y, z+1$
iv	$1-x, \frac{1}{2}+y, \frac{3}{2}-z$	v	$\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$	vi	$x, y+1, z$
vii	$\frac{1}{2}-x, -y, -\frac{1}{2}+z$	viii	$\frac{1}{2}-x, 1-y, \frac{1}{2}+z$	ix	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
X-H...Y		X...Y	X-H	H...Y	\angle X-H...Y
O(8)-H(O8)	$W(6)^i$	2.556 Å	0.919 Å	1.744 Å	145.9°
O(3')-H(O3')	O(7) ⁱⁱ	2.698	0.881	1.824	174.7
N(6)-H(6)	N(3) ⁱⁱⁱ	2.993	0.816	2.278	148.5
N(6)-H'(6)	O(1') ^{iv}	3.045	1.000	2.100	157.0
$W(1)$ -H($W1$) ^v	O(6) ^v	2.910	0.774	2.150	167.2
$W(1)$ -H'($W1$) ^v	$W(3)$ ^{vi}	2.856	1.126	1.862	144.7
$W(2)$ -H($W2$)	O(6) ^{vii}	2.840	0.770	2.106	159.7
$W(2)$ -H'($W2$)	$W(3)$	2.798	0.888	1.912	176.3
$W(3)$ -H($W3$)	O(6)	2.784	0.992	1.863	153.0
$W(3)$ -H'($W3$)	O(7) ⁱⁱ	2.883	1.000	1.962	151.8
$W(4)$ -H($W4$) ^{viii}	O(8) ^{viii}	2.858	0.901	2.020	154.1
$W(5)$ -H($W5$)	$W(4)$ ^v	2.829	1.019	1.913	148.0
$W(6)$ -H($W6$)	O(3')	2.768	0.859	2.063	138.9
$W(6)$ -H'($W6$) ^{ix}	N(1) ^{ix}	2.786	1.050	1.742	172.0

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Structural Studies of Dibenz[*c,f*]azocines.III. 3-Bromo-*N*-methyl-5,6-dihydro-7*H*,12*H*-dibenz[*c,f*]azocine*†

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This X-ray study has shown that the compound C₁₆H₁₆NBr is 3-bromo-*N*-methyl-dibenzazocine. The crystals are monoclinic, *P*₂₁, with *a* = 16.398, *b* = 5.063, *c* = 8.038 Å, β = 92.07° and *Z* = 2. The structure has been determined from a Patterson map, and refined by least-squares calculations to *R* = 0.038 for the 1461 observed reflexions. The eight-membered azocine ring is in the rigid boat-chair conformation, with the N-CH₃ bond in an off-axial position. The dihedral angle between the planes of the two benzene rings is 114.5°. Substitution of Br in place of H on one of the benzene rings has increased the endocyclic C-C(Br)-C angle by 2.1°. The shortest Br...Br contact is 3.797 (1) Å. All the molecules in the crystal are of the same absolute configuration.

Introduction

The crystal structure of *N*-methyl-dihydro-dibenzazocine was described by Hardy & Ahmed (1974), as part I of this series. Its bromo derivative has been synthesized

by Renaud & Bovenkamp (1974) for the n.m.r. studies that they are conducting on the azocine system. The X-ray determination of the crystal structure has been undertaken in order to find out whether the compound is the 2-bromo (I) or the 3-bromo derivative (II). It was essential for the n.m.r. studies that the Br atom be *para* to the bridgehead methylene group.

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