

The Crystal and Molecular Structures of Oxoformycin B and Formycin B

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Oxoformycin B, $C_{10}H_{12}O_6N_4$, crystallizes in the orthorhombic space group $P2_12_12_1$ with $a=7.756$ (6), $b=21.313$ (15), $c=6.831$ (5) Å, $Z=4$, and formycin B, $C_{10}H_{12}O_5N_4$, in the monoclinic space group $P2_1$ with $a=13.493$ (10), $b=6.257$ (6), $c=6.705$ (5) Å, $\beta=99.71$ (7)°, $Z=2$. Both crystal structures were solved by the direct method and refined by the least-squares method to R values of 0.04 including H atoms. In oxoformycin B, the conformation of the C-glycosyl bond is *syn* with a χ angle of -164.1° and that of the ribofuranose group is C(3')-*endo* with a *gauche-gauche* (*gg*) conformation about the C(4')-C(5') bond. The *syn* conformation is stabilized by the intramolecular hydrogen bond, N(3)-H...O(5'). In formycin B, the corresponding conformations are *anti*, $\chi=30.4^\circ$, C(2')-*endo*-C(1')-*exo* and *gg*.

Introduction

Formycin B (FMB), an antibiotic having an inhibitory effect on the growth of *Xanthomonas oryzae*, was isolated from a culture filtrate of *Nocardia interforma* along with formycin (Hori, Ito, Takita, Koyama, Takeuchi & Umezawa, 1964; Koyama & Umezawa, 1965). Oxoformycin B (OXOFMB) is an oxidized metabolite of formycin or formycin B and its chemical structure was determined to be the 2,7-dione derivative (with the numbering system adopted in the present paper) of formycin B (Ishizuka, Sawa, Koyama, Takeuchi & Umezawa, 1967).

An X-ray structure determination of formycin was first carried out on its hydrobromide monohydrate

(Koyama, Maeda, Umezawa & Iitaka, 1966; Koyama, Umezawa & Iitaka, 1974) and a rare example of a *syn* conformation of the C-glycosyl bond was found. The conformation was further studied by Prusiner, Brennan & Sundaralingam (1973) using formycin monohydrate crystals. The present study was undertaken in order to elucidate the conformation of the related compounds and to compare them with that of formycin. A brief account of the structure determinations of formycin B and 3-deazaadenosine has been presented by Singh & Hodgson (1975).

Experimental

Crystals of OXOFMB and FMB were grown from aqueous solutions as colourless transparent plates with well developed faces of {010} in OXOFMB and {100} in FMB. The lattice constants and intensity data were

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Table 1. Crystal data, intensity measurement data and final R values

	Oxoformycin B (OXOFMB)	Formycin B (FMB)
	$C_{10}H_{12}O_6N_4$, M.W. 284.2	$C_{10}H_{12}O_5N_4$, M.W. 268.2
	m.p. 274°C (decomp.)	
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a	7.756 (6) Å	13.493 (10) Å
b	21.313 (15)	6.257 (6)
c	6.831 (5)	6.705 (5)
β		99.71 (7)°
U	1129.2 Å ³	557.96 Å ³
Z	4	2
D_x	1.672 g cm ⁻³	1.597 g cm ⁻³
D_m		1.60
Crystal size	0.07 × 0.22 × 0.22 mm	0.17 × 0.24 × 0.40 mm
Max. 2θ	140°	156°
Number of reflexions		
Observed	1153	1259
Theoretical	1300	1314
Final R	0.043	0.044

obtained on a Philips four-circle X-ray diffractometer using graphite-monochromated Cu $K\alpha$ radiation. Intensities were measured by a θ - 2θ scan method with the scan speed $\theta=4^\circ \text{ min}^{-1}$. For weaker reflexions with total counts less than 10^4 , repeated scans up to three

times were made. The background was counted at each end of the scan for half the total scan time. Weak reflexions with net peak intensities less than $2\sigma(I)$ were denoted as unobserved. Intensity measurement details are summarized in Table 1 along with crystal data.

Table 2. Final atomic parameters with estimated standard deviations in parentheses

The positional and thermal parameters for non-hydrogen atoms are multiplied by 10^4 . Positional parameters for H atoms are $\times 10^3$. The temperature factors for non-hydrogen atoms are of the form $T = \exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl) \}$, and for hydrogen atoms $T = \exp [-B(\sin \theta/\lambda)^2]$.

OXOFMB	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	1405 (5)	-947 (2)	1943 (7)	40 (7)	8 (1)	133 (10)	-1 (2)	4 (7)	5 (3)
C(2)	2550 (6)	-451 (2)	1649 (8)	48 (7)	9 (1)	96 (11)	-3 (2)	1 (9)	2 (3)
N(3)	1868 (5)	125 (2)	1351 (7)	34 (6)	7 (1)	128 (10)	-1 (2)	3 (7)	1 (3)
C(4)	97 (6)	206 (2)	1269 (8)	36 (7)	6 (1)	98 (11)	-2 (2)	0 (8)	0 (3)
C(5)	-990 (6)	-302 (2)	1457 (8)	39 (7)	6 (1)	115 (11)	0 (2)	2 (9)	0 (3)
C(6)	-399 (6)	-934 (2)	1774 (8)	47 (7)	8 (1)	120 (12)	-1 (2)	-1 (9)	1 (3)
N(7)	-2629 (6)	-79 (2)	1325 (7)	36 (6)	7 (1)	151 (11)	-1 (2)	-3 (8)	-1 (3)
N(8)	-2631 (5)	550 (2)	1075 (7)	42 (6)	7 (1)	137 (10)	1 (2)	-2 (8)	-1 (3)
C(9)	-968 (6)	732 (2)	1023 (7)	46 (7)	7 (1)	96 (11)	-1 (2)	5 (8)	-2 (3)
O(2)	4111 (4)	-560 (2)	1672 (6)	30 (5)	11 (1)	183 (10)	4 (2)	1 (7)	6 (3)
O(6)	-1271 (5)	-1407 (2)	1924 (6)	71 (6)	6 (1)	229 (11)	-5 (2)	-2 (8)	6 (3)
C(1')	-540 (6)	1415 (2)	792 (7)	32 (7)	8 (1)	86 (11)	-1 (2)	6 (8)	-1 (3)
C(2')	-757 (6)	1784 (2)	2730 (7)	57 (8)	5 (1)	90 (10)	5 (2)	5 (8)	-2 (3)
C(3')	1113 (7)	1850 (2)	3427 (7)	75 (8)	6 (1)	72 (10)	1 (2)	-5 (9)	-2 (3)
C(4')	2115 (6)	1901 (2)	1507 (8)	43 (8)	7 (1)	98 (11)	-3 (2)	3 (8)	-4 (3)
O(1')	1264 (4)	1460 (2)	228 (5)	48 (5)	9 (1)	93 (7)	-6 (2)	18 (6)	-11 (2)
O(2')	-1464 (5)	2385 (2)	2286 (5)	78 (6)	7 (1)	126 (9)	9 (2)	10 (7)	2 (2)
O(3')	1379 (5)	2374 (2)	4671 (5)	107 (7)	10 (1)	97 (8)	-2 (2)	-22 (7)	-11 (2)
C(5')	4023 (7)	1743 (2)	1586 (9)	55 (8)	8 (1)	168 (13)	-2 (3)	2 (10)	-1 (3)
O(5')	4215 (5)	1101 (2)	2240 (6)	48 (6)	9 (1)	191 (10)	6 (2)	13 (7)	2 (2)
	x	y	z	B		x	y	z	B
H(N1)	201 (10)	-135 (3)	270 (12)	7 (2)	H(C4')	207 (6)	239 (2)	102 (7)	1 (1)
H(N3)	256 (10)	51 (3)	138 (11)	6 (2)	H(O2')	-205 (9)	248 (3)	323 (10)	5 (2)
H(N7)	-366 (9)	-24 (3)	156 (10)	5 (2)	H(O3')	117 (7)	269 (2)	412 (8)	3 (1)
H(C1')	-139 (7)	158 (2)	-52 (8)	2 (1)	H(C5')	460 (8)	186 (3)	7 (9)	3 (1)
H(C2')	-163 (7)	153 (2)	375 (8)	2 (1)	H'(C5')	469 (7)	205 (2)	263 (9)	2 (1)
H(C3')	144 (7)	143 (2)	408 (8)	2 (1)	H(O5')	509 (7)	94 (2)	215 (8)	4 (1)
FMB									
N(1)	415 (3)	700 (0)	2155 (5)	32 (2)	102 (10)	83 (7)	-2 (5)	-15 (3)	-13 (9)
C(2)	635 (3)	-1100 (9)	3221 (7)	33 (3)	89 (13)	126 (10)	-6 (5)	-12 (4)	-16 (10)
N(3)	1166 (3)	-1229 (7)	5043 (5)	34 (2)	65 (10)	96 (8)	-6 (4)	-13 (3)	-6 (7)
C(4)	1494 (3)	751 (8)	5817 (6)	23 (2)	68 (10)	79 (8)	-3 (5)	-10 (3)	-12 (9)
C(5)	1320 (3)	2662 (8)	4794 (6)	27 (2)	74 (11)	80 (8)	4 (4)	-13 (3)	-7 (9)
C(6)	752 (3)	2755 (8)	2762 (6)	32 (3)	96 (13)	83 (8)	8 (5)	-11 (4)	-19 (9)
N(7)	1763 (3)	4221 (7)	6036 (5)	44 (2)	59 (10)	82 (8)	-3 (4)	-20 (3)	3 (8)
N(8)	2204 (3)	3400 (7)	7860 (5)	37 (2)	85 (10)	82 (7)	-5 (4)	-21 (3)	-1 (8)
C(9)	2046 (3)	1287 (7)	7733 (6)	25 (2)	85 (13)	79 (8)	0 (4)	-9 (4)	5 (8)
O(6)	559 (3)	4330 (6)	1685 (5)	64 (3)	89 (9)	97 (7)	14 (4)	-29 (3)	6 (7)
C(1')	2458 (3)	-290 (8)	9330 (6)	27 (2)	94 (12)	54 (8)	-1 (4)	-7 (3)	5 (8)
C(2')	3515 (3)	-1094 (8)	9150 (6)	26 (2)	103 (12)	79 (8)	2 (5)	-1 (3)	1 (9)
C(3')	3836 (3)	-2102 (8)	11239 (6)	31 (3)	101 (14)	96 (9)	8 (5)	-11 (4)	12 (9)
C(4')	3325 (3)	-659 (8)	12629 (6)	23 (2)	122 (13)	73 (8)	-2 (5)	-9 (3)	24 (9)
O(1')	2578 (2)	616 (7)	11303 (4)	29 (2)	146 (9)	61 (6)	25 (4)	-6 (2)	-3 (7)
O(2')	3456 (2)	-2539 (7)	7502 (4)	35 (2)	134 (9)	100 (7)	3 (4)	5 (3)	-27 (8)
O(3')	3464 (3)	-4255 (7)	11300 (5)	63 (2)	86 (8)	132 (8)	-1 (5)	-25 (4)	27 (8)
C(5')	4014 (3)	900 (10)	13910 (7)	33 (3)	146 (14)	97 (9)	-10 (6)	-11 (4)	9 (11)
O(5')	4559 (2)	2201 (7)	12720 (5)	30 (2)	127 (10)	189 (9)	-7 (4)	-3 (3)	29 (9)
	x	y	z	B		x	y	z	B
H(N1)	-12 (5)	82 (16)	125 (10)	8 (2)	H(C3')	471 (4)	-206 (11)	1153 (8)	4 (1)
H(C2)	20 (4)	-236 (13)	279 (9)	5 (2)	H(O3')	311 (6)	-459 (16)	1047 (11)	9 (2)
H(N7)	171 (5)	539 (14)	579 (10)	6 (2)	H(C4')	292 (4)	-161 (10)	1356 (8)	3 (1)
H(C1')	200 (4)	-140 (10)	921 (8)	3 (1)	H(C5')	349 (4)	201 (12)	1475 (9)	4 (1)
H(C2')	397 (4)	23 (11)	893 (8)	3 (1)	H'(C5')	439 (4)	14 (12)	1492 (10)	5 (2)
H(O2')	407 (4)	-274 (13)	733 (8)	4 (1)	H(O5')	430 (5)	307 (13)	1216 (10)	7 (2)

Determination and refinement of the structures

Both structures were determined by the symbolic addition method and refined by the block-diagonal least-squares method with *HBL5* (Okaya & Ashida, 1967).

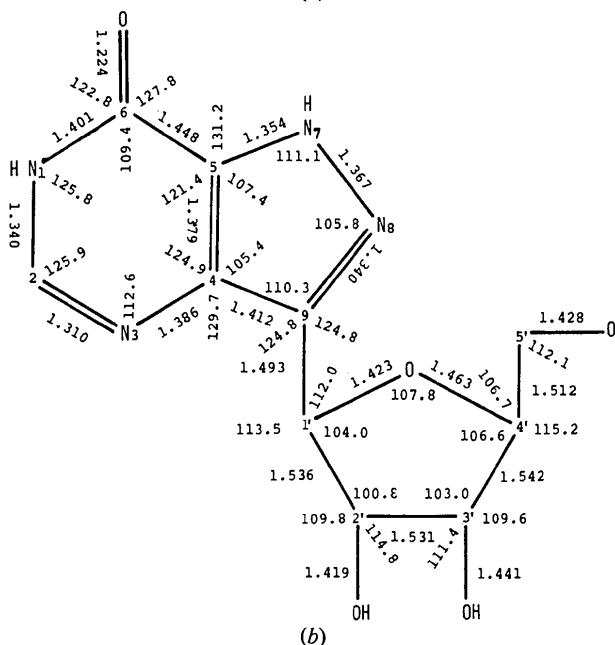
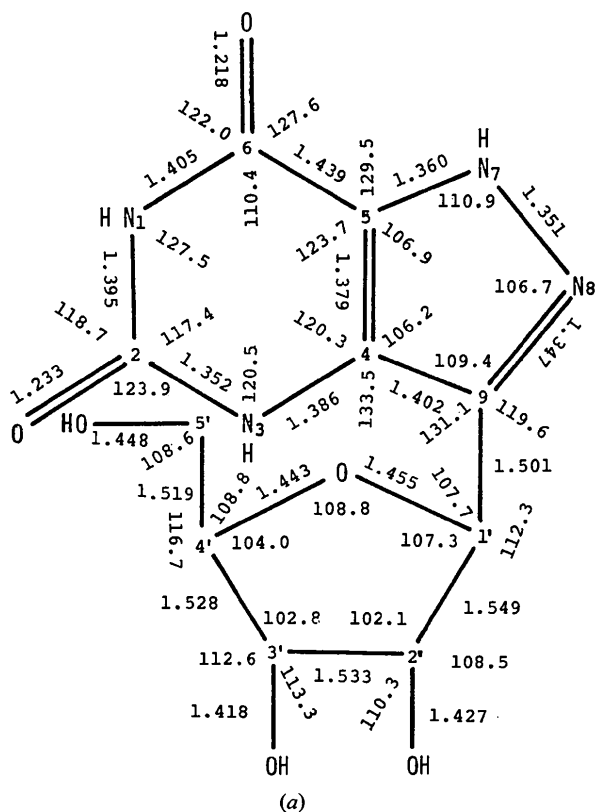


Fig. 1. Chemical structures of (a) OXOFMB and (b) FMB with bond lengths (Å) and bond angles (°).

Unit weight was assigned for each reflexion. All the H atoms were located on the difference electron-density maps and their coordinates and isotropic temperature factors were also refined. The final *R* values are listed in Table 1. The atomic scattering factors for C, N and O were those given in *International Tables for X-ray Crystallography* (1962) as SX-6, 7 and 8, respectively and for H, from Stewart, Davidson & Simpson (1965). The atomic parameters are given in Table 2.*

Discussion of the structure

Molecular structure

The chemical structures of OXOFMB and FMB are given in Fig. 1(a) and (b), showing the numbering of atoms and the protonated sites of the bases, which will be mentioned in the following discussions. The bond lengths and bond angles are also shown in Fig. 1. Comparison of the lengths (Table 3), angles (Table 4) and conformations with those found in formycin hydrobromide monohydrate (FM.HBr; Koyama, Umezawa & Iitaka, 1974) and formycin monohydrate (FM; Prusiner, Brennan & Sundaralingam, 1973) shows that:

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31302 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Comparison of bond lengths in formycins (Å)

	OXOFMB	FMB	FM.HBr(1)	FM.H ₂ O(2)
Pyrimidine group				
N(1)–C(2)	1.395 (6)	1.340 (5)	1.412	1.355
C(2)–N(3)	1.352 (6)	1.310 (5)	1.284	1.313
N(3)–C(4)	1.386 (6)	1.386 (6)	1.367	1.374
C(4)–C(5)	1.379 (6)	1.379 (7)	1.417	1.379
C(5)–C(6)	1.439 (6)	1.448 (5)	1.391	1.420
C(6)–N(1)	1.405 (6)	1.401 (5)	1.364	1.336
C(6)–O(6)	1.218 (6)	1.224 (6)	1.314*	1.334*
C(2)–O(2)	1.233 (6)	—	—	—
Pyrazole group				
C(5)–N(7)	1.360 (6)	1.354 (6)	1.351	1.359
N(7)–N(8)	1.351 (6)	1.367 (5)	1.350	1.363
N(8)–C(9)	1.347 (6)	1.340 (6)	1.362	1.324
C(9)–C(4)	1.402 (6)	1.412 (6)	1.389	1.426
C(9)–C(1')	1.501 (6)	1.493 (6)	1.492	1.501
Ribofuranose group				
C(1')–C(2')	1.549 (7)	1.536 (6)	1.548	1.535
C(1')–O(1')	1.455 (6)	1.423 (5)	1.408	1.438
C(2')–C(3')	1.533 (7)	1.531 (6)	1.512	1.533
C(2')–O(2')	1.427 (6)	1.419 (6)	1.392	1.407
C(3')–C(4')	1.528 (7)	1.542 (7)	1.522	1.538
C(3')–O(3')	1.418 (6)	1.441 (7)	1.422	1.431
C(4')–O(1')	1.443 (6)	1.463 (5)	1.468	1.453
C(4')–C(5')	1.519 (7)	1.512 (7)	1.494	1.499
C(5')–O(5')	1.448 (6)	1.428 (7)	1.445	1.428
Average e.s.d.			0.015	0.005

* C–N bond length.

(1) Koyama, Umezawa & Iitaka (1974). (2) Prusiner, Brennan & Sundaralingam (1973).

Table 4. Comparison of bond angles in formycins

	OXOFMB	FMB	FM.HBr(1)	FM.H ₂ O(2)
Pyrimidine group				
C(2)–N(1)–C(6)	127.5°	125.8°	123°	119.1°
N(1)–C(2)–N(3)	117.4	125.9	125	129.0
N(1)–C(2)–O(2)	118.7	—	—	—
O(2)–C(2)–N(3)	123.9	—	—	—
C(2)–N(3)–C(4)	120.5	112.6	114	112.5
N(3)–C(4)–C(5)	120.3	124.9	125	123.0
C(4)–C(5)–C(6)	123.7	121.4	119	119.9
C(5)–C(6)–N(1)	110.4	109.4	115	116.4
C(5)–C(6)–O(6)	127.6	127.8	126*	123.1*
O(6)–C(6)–N(1)	122.0	122.8	120†	120.5†
Pyrazole group				
C(5)–C(4)–C(9)	106.2	105.4	104	105.5
N(3)–C(4)–C(9)	133.5	129.7	132	131.5
C(4)–C(5)–N(7)	109.6	107.4	113	107.0
C(6)–C(5)–N(7)	129.5	131.2	128	131.1
C(5)–N(7)–N(8)	110.9	111.1	103	110.9
N(7)–N(8)–C(9)	106.7	105.8	114	106.8
N(8)–C(9)–C(4)	109.4	110.3	107	109.8
N(8)–C(9)–C(1')	119.6	124.8	123	121.9
C(4)–C(9)–C(1')	131.1	124.8	131	128.2
Ribofuranose group				
C(1')–O(1')–C(4')	108.8	107.8	110	109.3
C(2')–C(1')–C(9)	112.3	113.5	116	115.2
C(2')–C(1')–O(1')	107.3	104.0	106	103.4
C(9)–C(1')–O(1')	107.7	112.0	109	109.4
C(3')–C(2')–C(1')	102.1	100.8	101	102.3
C(3')–C(2')–O(2')	110.3	114.8	116	114.7
C(1')–C(2')–O(2')	108.5	109.8	110	114.6
C(4')–C(3')–C(2')	102.8	103.0	102	102.7
C(4')–C(3')–O(3')	112.6	109.6	111	108.9
C(2')–C(3')–O(3')	113.3	111.4	108	111.6
O(1')–C(4')–C(3')	104.0	106.6	105	106.9
O(1')–C(4')–C(5')	108.8	106.7	109	108.9
C(3')–C(4')–C(5')	116.7	115.2	113	112.3
O(5')–C(5')–C(4')	108.6	112.1	111	111.6
Average e.s.d.	0.4	0.4	1	0.3

* C–C–N bond angle.

† N–C–N bond angle.

(1) Koyama, Umezawa & Iitaka (1974). (2) Prusiner, Brennan & Sundaralingam (1973).

(1) C(6)–C(5) and C(6)–N(1) in FMB and OXOFMB and C(2)–N(1) and C(2)–N(3) in OXOFMB, all of which involve oxygen-substituted ring carbon atoms, are significantly longer and the endocyclic bond angles subtended at these C atoms are several degrees smaller than those at the corresponding C atoms in FM.HBr and FM. A similar effect was also observed in caffeine (Sutor, 1958*b*) and theophylline (Sutor, 1958*a*) at C(2) and C(6).

(2) The bond angles subtended at the protonated N atoms, N(1) and N(7) in OXOFMB and FMB and N(3) in OXOFMB, are several degrees greater than those at the unprotonated N atoms. This effect has already been pointed out by Sundaralingam & Jensen (1965), Singh (1965), Rao & Sundaralingam (1970) and Prusiner *et al.* (1973).

(3) The deviations of atoms from the least-squares planes through the base atoms (Table 5) show that the bases are not planar. However, the pyrazole ring is

Table 5. Least-squares plane through the base atoms and atom deviations

The equation of the plane is $AX + BY + CZ = D$, where X, Y and Z are measured in Å and $X||a^*$, $Y||b$ and $Z||c$.

	OXOFMB	FMB
N(1)	0.053 Å	0.037 Å
C(2)	–0.011	0.004
N(3)	–0.015	–0.024
C(4)	–0.010	–0.012
C(5)	–0.023	–0.014
C(6)	–0.022	–0.015
N(7)	–0.009	–0.012
N(8)	0.023	0.021
C(9)	0.013	0.016
O(2)*	–0.060	—
O(6)*	–0.054	–0.038
C(1')*	0.065	–0.052
<i>A</i>	–0.0255	0.8435
<i>B</i>	0.1493	–0.1186
<i>C</i>	0.9885	–0.5238
<i>D</i>	0.930	–0.257
θ^\dagger	8°42'	58°25'

* These atoms are not included in the least-squares calculation.

† Inclination angle of the normal of the base plane to the *c* axis.

planar within ± 0.003 Å. The deviations of C(5) and C(6) and in particular N(1) are remarkable. In OXOFMB, FMB and FM, C(1') deviates from the base plane by about 0.05 Å but in FM.HBr the deviation is as much as 0.140 Å. Therefore, there seems to be no correlation between the deviation of C(1') and the conformation of the glycosyl bond.

(4) The conformation about the C-glycosyl bond can be described by the χ angle (Sundaralingam, 1969). The values of χ lie in the *syn* range in OXOFMB, FM.HBr and FM while in FMB the value is in the *anti* range (Table 6). The conformation of the molecules may be clearly seen in the stereoscopic drawings in Fig. 2(*a*) and (*b*). As seen in Table 6, the conformation of FMB can be classified as high *anti* while that of FM as intermediate (*anti-syn*). A high or intermediate value of χ or the rotation of the C(5')–O(5') bond away from the *gauche-gauche* conformation is the necessary condition to alleviate the repulsion between the negatively charged N(8) and O(5') atoms (Prusiner *et al.*, 1973). The *syn* conformation in OXOFMB and FM.HBr is stabilized by the intramolecular hydrogen bond between N(3) and O(5').

(5) Exocyclic bond angles at the glycosyl bond, N(8)–C(9)–C(1') and C(4)–C(9)–C(1'), are symmetric in FMB while in OXOFMB, FM.HBr and FM which have the *syn* glycosyl bond, they are markedly dissymmetric and the latter angle is widened to about 130°.

(6) In the *syn* conformers, the bond angle C(9)–C(1')–O(1') is smaller while N(3)–C(4)–C(9) is larger by a few degrees than those of the *anti* conformer. The steric interactions between the ribose and base groups seem to be considerably relieved by the deformations mentioned above.

Table 6. Torsional angles and the displacement of atoms in the furanose ring

	OXOFMB	FMB	FM.HBr (1)	FM.H ₂ O(2)
Torsional angle				
χ [N(8)-C(9)-C(1')-O(1')]	-164.1°	30.4°	-149.3°	109.8°
Conformation about the glycosyl bond	<i>syn</i>	<i>anti</i>	<i>syn</i>	<i>syn</i>
τ_0 [O(1')-C(1')]	-8.2	-34.8	-10.6	-30.6
τ_1 [C(1')-C(2')]	-16.3	42.5	31.3	39.4
τ_2 [C(2')-C(3')]	33.1	-33.5	-38.9	-33.1
τ_3 [C(3')-C(4')]	-39.2	14.4	33.7	15.7
τ_4 [C(4')-O(1')]	29.6	12.7	-14.4	9.4
Puckering of the furanose ring	C(3')- <i>endo</i>	C(2')- <i>endo</i> - C(1')- <i>exo</i>	C(2')- <i>endo</i> - C(1')- <i>exo</i>	C(2')- <i>endo</i> - C(1')- <i>exo</i>
φ_{oo} [O(1')-C(4')-C(5')-O(5')]	-57.2°	-63.9°	46.6°	57.6°
φ_{oc} [C(3')-C(4')-C(5')-O(5')]	60.0	54.2	162.4	175.8
Conformation about the C(4')-C(5') bond	<i>gg</i>	<i>gg</i>	<i>gt</i>	<i>gt</i>
Displacement of atoms from the least-squares plane				
C(1')	-0.044 Å	-0.298* Å	0 Å	-0.221* Å
C(2')	0.026	0.0370*	0.273*	0.406*
C(3')	0.574*	0	-0.367*	0
C(4')	-0.029	0	0	0
O(1')	0.046	0	0	0

* These atoms are not included in the least-squares calculations.

(1) Koyama, Umezawa & Iitaka (1974). (2) Prusiner, Brennan & Sundaralingam (1973).

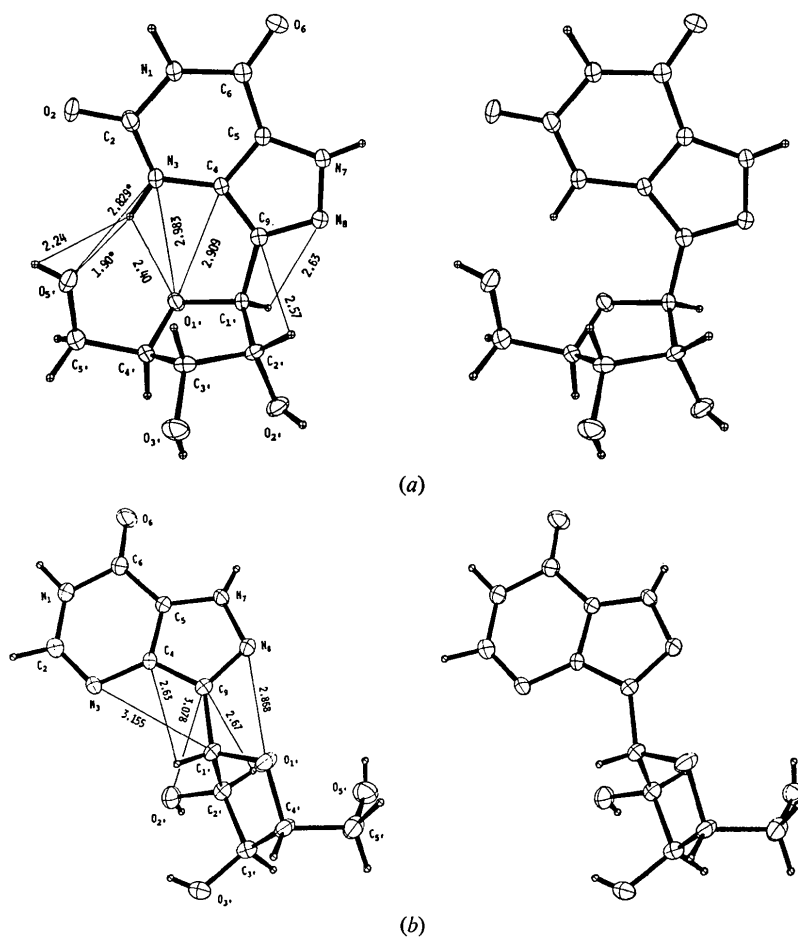


Fig. 2. Stereoscopic view of the molecules of (a) OXOFMB and (b) FMB drawn by ORTEP (Johnson, 1965). Non-hydrogen atoms are shown as ellipsoids of 50% probability and hydrogen atoms as spheres of arbitrary scale. Some shortest intramolecular contact distances are also shown. An asterisk indicates an intramolecular hydrogen bond.

(7) The lengths of C(1')-O(1') and C(4')-O(1') in FMB are in the usual range (Arnott & Hukins, 1972). However, in OXOFMB, the former is lengthened to 1.455 Å, which is 0.012 Å longer than the latter and exhibits a reversed order of magnitude as compared with usual nucleosides and nucleotides (Sundaralingam, 1965).

(8) The conformation of the ribofuranose group is shown in Table 6. The ring conformation in FMB as represented by the τ angles and by the displacement of atoms, is very similar to that in FM, while OXOFMB adopts a quite different conformation of C(3')-endo. In the C(3')-endo form of purine nucleosides, close contacts of N(3) with either H(C3') or O(1') occur around $\chi = -100^\circ$ or -170° , respectively, which limit the allowed ranges of χ to $140 \sim 85^\circ$ and $60 \sim -10^\circ$ but if contact radii 0.1 Å shorter than the normal values are permissible, these ranges extend to $150 \sim -20^\circ$ and an additional allowed range in the *syn* region, $-140 \sim -150^\circ$, appears [Haschemeyer & Rich (1967); these authors assumed the structural parameters of adenosine-5'-phosphate and their ϕ_{CN} angle is approximately identical with $-\chi$]. The *syn* conformation with $\chi = -164^\circ$ found in OXOFMB may therefore be said to be a rare case for C(3')-endo puckering of the ribofuranose ring. However, the intramolecular contact distances listed in Table 7 show that there is no particularly short distance between the base and ribose groups although the distances N(3)···O(1'), 2.983 Å, and H(N3)···O(1'), 2.40 Å, are nearly at the limit of normal intramolecular contact distances. In Fig. 2, some short distances are marked by thin lines. The rare conformation found in OXOFMB may be explained by the attractive forces between protonated N(3) and the electronegative atoms in ribose. Thus the N(3)H group not only forms a rather strong intramolecular hydrogen bond to O(5') but also attracts O(1') near to H(N3). The χ angle is then forced to take a large value in order to achieve the *cis* disposition of N(3) with respect to O(1') around the glycosyl bond. Under these circumstances, the *gg* conformation mentioned below will bring O(5') close to H(N3) and nearly

Table 7. Intramolecular contact distances between the atoms in the base and in ribose

The distances less than 3.2 Å for A···A, 2.8 Å for A···H and 2.4 Å for H···H are listed, where A and H denote non-hydrogen and hydrogen atoms respectively.

OXOFMB		FMB	
N(3)···O(1')	2.983 (5) Å	N(3)···C(1')	3.155 (5)
H(N3)···O(1')	2.40 (7)	C(4)···H(C1')	2.63 (5)
*N(3)···O(5')	2.829 (5)	N(8)···O(1')	2.868 (5)
*H(N3)···O(5')	1.90 (7)	C(9)···O(2')	3.078 (6)
H(N3)···H(O5')	2.24 (9)	C(9)···H(C2')	2.67 (5)
C(4)···O(1')	2.909 (6)		
N(8)···H(C1')	2.63 (5)		
C(9)···H(C2')	2.57 (5)		

* Hydrogen bond.

on a line connecting N(3) and H(N3), resulting in the formation of the intramolecular hydrogen bond.

(9) The conformation about C(4')-C(5') in OXOFMB and FMB is *gauche-gauche* (*gg*) which is more common in nucleosides and nucleotides than the *gauche-trans* (*gt*) conformation found in FM. HBr and FM. The *gg* conformation in OXOFMB is a consequence of the strong interactions described in (8).

Crystal structures

The crystal structures of OXOFMB and FMB are shown in Fig. 3(a) and (b) in *c* axis projections. In both crystals, the molecules are held together mainly by hydrogen bonds. The lengths and angles associated with these hydrogen bonds are listed in Table 8. Most of them link the ribose group to either the bases or the ribose groups. Some of the bonds link the bases to each other; N(7)-H···O(2) in OXOFMB, and N(1)-H···O(6) and N(7)-H···N(3) in FMB. There is not, however, more than one bond connecting a pair of bases. This feature of the hydrogen bonding between the bases is different from that found in double helical polynucleotides.

Table 8. Hydrogen-bond lengths and angles

OXOFMB

Symmetry operations are: (i) x, y, z ; (ii) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (iii) $-1 + x, y, z$; (iv) $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (v) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $1 - x, y, z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$.

Atom 1	Atom 2	Atom 3	Distance		Angle
			1-3	2-3	3-1-2
*N(3)-H(N3)···O(5')			2.829 (5) Å	1.90 (7) Å	13 (4)°
N(1)-H(N1)···O(1 ⁱⁱⁱ)			3.082 (5)	2.20 (8)	31 (4)
N(7)-H(N7)···O(2 ⁱⁱⁱ)			2.739 (6)	1.86 (7)	6 (4)
O(2')-H(O2')···O(3' ^{iv})			2.717 (5)	1.91 (7)	5 (5)
O(3')-H(O3')···O(6')			2.818 (5)	2.06 (5)	13 (4)
O(5')-H(O5')···N(8 ^{vi})			2.828 (5)	2.09 (5)	12 (4)

FMB

Symmetry operations are: (i) x, y, z ; (ii) $-x, -\frac{1}{2} + y, -z$; (iii) $x, 1 + y, z$; (iv) $x, -1 + y, z$; (v) $1 - x, -\frac{1}{2} + y, 2 - z$; (vi) $-x, \frac{1}{2} + y, 1 - z$; (vii) $x, y, -1 + z$.

N(1)-H(N1)···O(6 ⁱⁱ)	2.820 (4)	2.17 (7)	35 (5)
N(7)-H(N7)···N(3 ⁱⁱⁱ)	3.003 (6)	2.27 (9)	10 (6)
O(2')-H(O2')···O(5' ^v)	2.712 (5)	1.85 (6)	7 (4)
O(3')-H(O3')···N(8 ^{iv})	3.007 (5)	2.32 (8)	13 (7)
O(5')-H(O5')···O(3' ⁱⁱⁱ)	2.745 (6)	2.05 (8)	12 (6)

* Intramolecular hydrogen bond.

Other close approaches of atoms between the neighbouring molecules can be seen in Table 9 and Fig. 3(a) and (b). In OXOFMB, interactions between (i) and (ii) (related by a screw diad axis along *c*) which involve the carbonyl group, C(2)=O(2), are remarkable while in FMB, those between (i) and (vi) (related by a screw diad axis along *b*) and also between (i) and (vii) (translated in *c*) are remarkable (the former involves the carbonyl group, C(6)=O(6) and the latter O(1') of the ribose group).

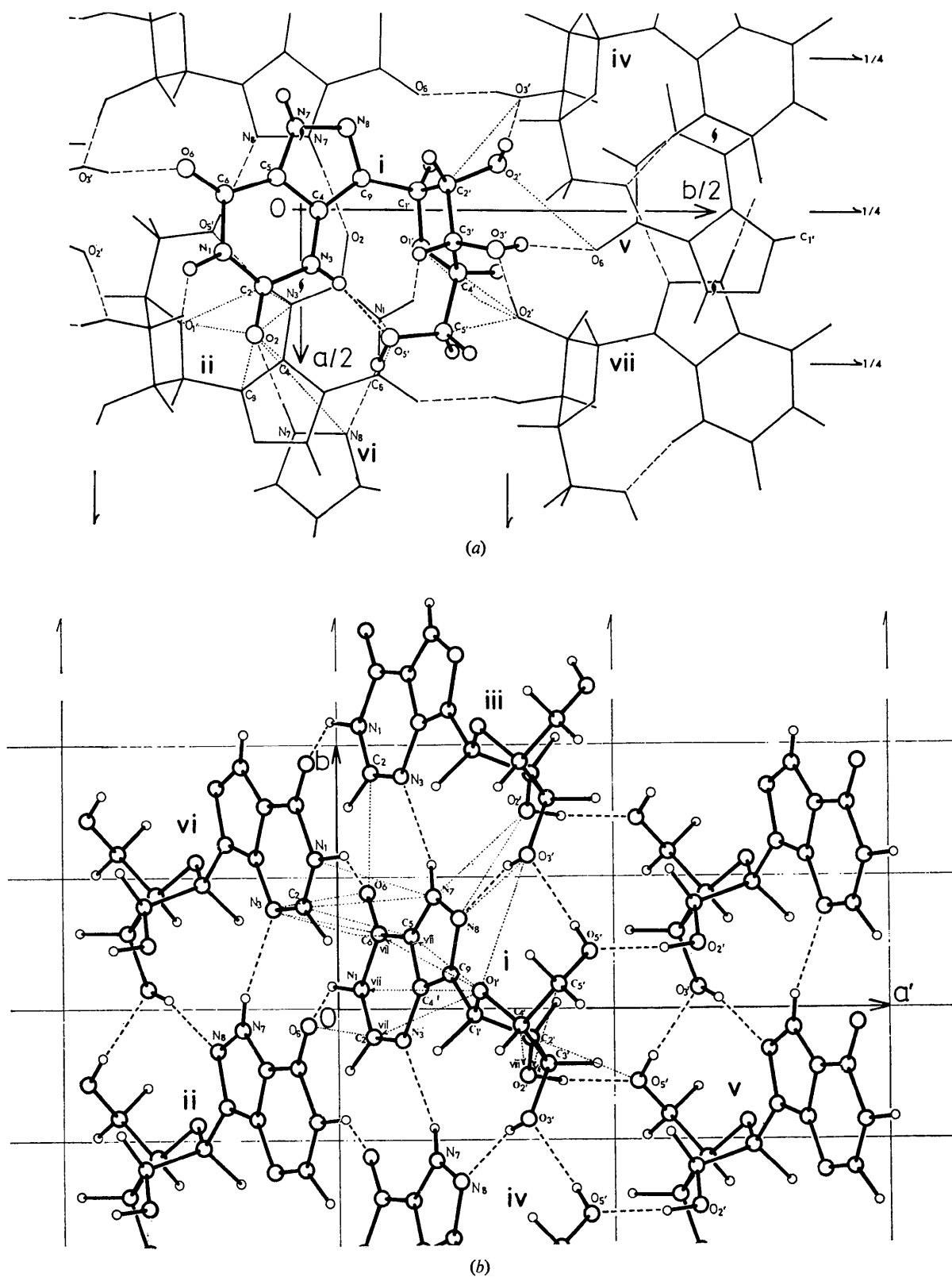


Fig. 3. Projections of the crystal structures along the c axis. (a) OXOFMB. (b) FMB. Hydrogen bonds are shown by broken lines and other intermolecular short distances less than 3.5 \AA between non-hydrogen atoms are shown by dotted lines. Symmetry codes are defined in Table 8.

Table 9. *Intermolecular distances less than 3.5 Å*

Hydrogen atoms are not included. Symmetry operations are listed in Table 8.

OXOFMB		FMB	
C(2)····N(3 ⁱⁱ)	3.317 (7) Å	C(2)····O(6 ⁱⁱ)	3.421 (5) Å
C(2)····O(1 ⁱⁱⁱ)	3.383 (6)	C(5)····C(2 ^{vi})	3.243 (7)
O(2)····N(3 ⁱⁱ)	3.413 (6)	C(5)····N(3 ^{vi})	3.446 (6)
O(2)····C(4 ⁱⁱ)	3.288 (7)	C(6)····N(2 ^{vi})	3.248 (6)
O(2)····N(8 ^{vi})	3.486 (5)	O(6)····C(2 ⁱⁱⁱ)	3.035 (7)
O(2)····C(9 ⁱⁱ)	3.323 (6)	O(6)····N(3 ^{vi})	3.476 (6)
O(2)····O(1 ⁱⁱⁱ)	3.108 (5)	N(7)····N(1 ^{vi})	3.488 (6)
O(1')····O(2 ^{vii})	3.481 (5)	N(7)····C(2 ^{vi})	3.363 (6)
C(2')····O(3 ^{iv})	3.363 (6)	N(7)····O(2 ⁱⁱⁱ)	3.088 (5)
O(2')····O(6 ^v)	3.378 (5)	N(8)····O(2 ⁱⁱⁱ)	3.083 (6)
C(4')····O(2 ^{vii})	3.201 (6)	N(8)····O(3 ⁱⁱⁱ)	3.007 (5)
C(5')····O(2 ^{vii})	3.254 (7)	O(1')····N(1 ^{vi})	3.067 (5)
O(5')····N(1 ⁱⁱ)	3.265 (6)	O(1')····C(2 ^{vi})	3.288 (6)
O(5')····C(6 ⁱⁱ)	3.250 (7)	O(1')····C(5 ^{vii})	3.367 (6)
		O(1')····C(6 ^{vii})	3.104 (6)
		O(1')····O(3 ⁱⁱⁱ)	3.425 (6)
		C(2')····O(5 ^v)	3.250 (6)
		C(4')····O(2 ^{vii})	3.449 (5)
		C(5')····O(2 ^{vii})	3.408 (6)

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The Crystal and Molecular Structure of (Pentahaptofluorenyl)(trihaptofluorenyl)dichlorozirconium(IV)

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(Pentahaptofluorenyl)(trihaptofluorenyl)dichlorozirconium(IV), f_2ZrCl_2 , (fl = fluorenyl) is monoclinic, space group $P2_1/n$, with $a = 12.347$, $b = 13.771$, $c = 11.922$ Å, $\beta = 98.2^\circ$, $Z = 4$. The structure was solved by the heavy-atom technique and refined by least-squares methods with 2697 independent reflexions to give $R = 0.053$. The normally tetrahedral coordination of two h^5 -bonded ligands and two Cl atoms is distorted to the extent that the bonding of one fluorenyl group is reduced to an h^3 system, that the fl–Zr–fl angle is opened out to 125.0° , and that the Cl–Zr–Cl angle is closed down to 93.6° .

Introduction

The reaction of ZrCl_4 and sodium fluorenyl in diethoxyethane gave orange prisms on sublimation of the evaporated reaction mixture. The complex is insoluble in most organic solvents and shows reactivity towards others (e.g. THF). It is an efficient catalyst (in combination with aluminum alkyls) for olefin polym-

erization (Wailes & Weigold, 1974). These unusual properties prompted an X-ray investigation to obtain information about its geometry and type of bonding. A preliminary report of its preparation and structure has been published (Kowala, Wailes, Weigold & Wunderlich, 1974).

Experimental

The space group and preliminary cell dimensions were determined from Weissenberg photographs. Accurate cell parameters were based on high-order reflexions,

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