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Crystal and Molecular Structure of an Oxygenated Dimer of 3-Methylindole, (5aα,10bα,11aβ,12β)-6-Acetyl-5a,10b,11a,12-tetrahydro-10b,12-dimethyl-6*H*-oxazolo[3,2-*a*:4,5-*b*′]diindol-12-ol

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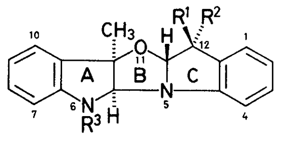
The crystal structure of the title compound (1b), which is the acetyl derivative of one of the oxygenated dimers of 3-methylindole, has been determined by single-crystal X-ray analysis. The crystals are monoclinic, space group $P2_1/a$, with $a = 13.980$ (3), $b = 12.340$ (3), $c = 10.021$ (4) Å, $\beta = 92.51$ (3)°, and $Z = 4$. The bond lengths and angles in 1b are not much different from those in the stereoisomer of 1b with inverted configuration at the C_{12} position, indicating the rigidity of the five successive ring structures of 6*H*-oxazolo[3,2-*a*:4,5-*b*′]diindole. The molecular stereochemistries of these isomers are discussed.

Keywords X-ray analysis; molecular structure; crystal structure; 6*H*-oxazolo[3,2-*a*:4,5-*b*′]diindole

In the previous papers,[1,2] we reported that the catalytic oxygenation of 3-methylindole with a Co(II) Schiff-base complex, *N*,*N*′-(*cis*-1,2-cyclohexylene)bis(3-*tert*-butylsalicylideneaminato)cobalt(II), yielded two novel oxygenated dimers of the substrate (**1a** and **2a**) besides 2-formylaminoacetophenone as the major product. The structure of **2a** was unequivocally established by the X-ray crystallographic analysis of the N-acetyl derivative (**2b**).[1] However, the structure of **1a** was deduced based primarily on the spectral data of **1a** and its N-acetyl derivative (**1b**).[2]

These oxygenated dimers have a novel C_6–C_4N–C_3NO–C_4N–C_6 ring system derived from 6*H*-oxazolo[3,2-*a*:4,5-*b*′]diindole, no derivative of which has previously been reported. The structural study of these isomers should provide information about the influence of the substituents at C_{12} on the ring structure. In order to confirm the structure of **1** and to get information about the geometry of this ring system, the X-ray crystal structure analysis of **1b** has been carried out.



1a: $R^1 = OH$, $R^2 = CH_3$, $R^3 = H$
1b: $R^1 = OH$, $R^2 = CH_3$, $R^3 = COCH_3$
2a: $R^1 = CH_3$, $R^2 = OH$, $R^3 = H$
2b: $R^1 = CH_3$, $R^2 = OH$, $R^3 = COCH_3$

Chart 1

Experimental

X-Ray Structure Analysis Colorless transparent prisms of **1b** were obtained by slow evaporation of an ethanol–hexane solution at room temperature. A crystal with approximate dimensions of 0.68 × 0.32 × 0.30 mm was used. The unit-cell parameters and intensity data were measured on an Enraf-Nonius CAD-4 automated four-circle diffractometer at the Faculty of Pharmaceutical Sciences, Nagoya City University, with graphite-monochromated Cu K_α radiation ($\lambda = 1.54184$ Å). Crystal data are: $C_{20}H_{20}N_2O_3$, $M_r = 336.39$, monoclinic, space group $P2_1/a$, $a = 13.980(3)$ Å, $b = 12.340(3)$ Å, $c = 10.021(4)$ Å, $\beta = 92.51(3)°$, $V = 1727.1(9)$ Å^3, $Z = 4$, $D_x = 1.294$ g cm^{-3}, $D_m = 1.289$ g cm^{-3} (flotation in aqueous KI solution), and μ(Cu K_α) = 6.71 cm^{-1}. Intensity data were collected using the ω–2θ scan technique within the range of $3° < 2\theta < 120°$. A total of 2821 reflections (2712 independent reflections) were obtained; of these, 2056 reflections having $F_o > 3\sigma(F_o)$ were used for the structure analysis. No correction for absorption was made.

The structure was solved by the direct method using the program MULTAN82,[3] and refined by a full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. All the hydrogen atoms were located by difference Fourier syntheses. The quantity minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 4F_o/\sigma^2(F_o)$. The final refinement converged with $R = 0.072$ and $R_w = 0.089$ for 2056 reflections. Calculations were done on a MicroVAX II computer using the SDP program package.[4] Atomic scattering factors taken from reference 5 were used on the SDP. Figures 1 and 2 were drawn by the use of the ORTEP program[6] with an ACOS 930 computer at the Computer Center of Nagoya City University.

Results and Discussion

The final atomic positional and thermal parameters for non-hydrogen atoms of **1b** are given in Table I. Stereoscopic drawings of the molecules **1b** and **2b** are shown in Fig. 1, together with the atomic numbering scheme. The molecular structure assigned to **1b** previously is thus confirmed. Dimers **1** and **2** are stereoisomers with different configurations only at the C_{12} position.

TABLE I. Fractional Atomic Coordinates (× 10⁴) and Thermal Parameters for Non-hydrogen Atoms of **1b**, with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}[a)]/Å^2
O(1)	3207 (2)	−293 (2)	4329 (2)	3.51 (5)
O(2)	4132 (2)	1385 (2)	1691 (2)	3.49 (5)
O(3)	−32 (2)	2071 (2)	3456 (3)	5.08 (6)
N(1)	993 (2)	685 (2)	3894 (3)	3.01 (6)
N(2)	2286 (2)	210 (2)	2495 (3)	2.64 (6)
C(1)	1196 (2)	922 (3)	5260 (3)	2.95 (7)
C(2)	783 (3)	1680 (3)	6075 (4)	4.11 (9)
C(3)	1130 (3)	1750 (4)	7389 (4)	4.9 (1)
C(4)	1852 (3)	1079 (4)	7886 (4)	5.1 (1)
C(5)	2259 (3)	325 (4)	7075 (4)	4.38 (9)
C(6)	1919 (2)	236 (3)	5747 (4)	3.20 (7)
C(7)	2252 (2)	−517 (3)	4705 (3)	2.94 (7)
C(8)	1618 (2)	−179 (3)	3438 (3)	2.84 (7)
C(9)	2202 (3)	−1703 (3)	5068 (4)	4.52 (9)
C(10)	374 (2)	1263 (3)	3064 (4)	3.38 (8)
C(11)	2592 (2)	−505 (3)	1477 (3)	2.78 (7)
C(12)	2032 (3)	−1195 (3)	680 (4)	3.58 (8)
C(13)	2478 (3)	−1768 (3)	−306 (4)	4.15 (9)
C(14)	3436 (3)	−1650 (3)	−514 (4)	3.83 (8)
C(15)	3998 (3)	−975 (3)	322 (4)	3.34 (8)
C(16)	3565 (2)	−405 (3)	1307 (3)	2.68 (7)
C(17)	3995 (2)	376 (3)	2343 (3)	2.81 (7)
C(18)	3167 (2)	490 (3)	3282 (3)	2.71 (7)
C(19)	4926 (2)	−25 (3)	3028 (4)	3.75 (8)
C(20)	204 (3)	846 (4)	1671 (4)	4.43 (9)

a) B_{eq}'s are the equivalent values of the anisotropic thermal parameters defined as: 4/3 $(B_{11}a^2 + B_{22}b^2 + B_{33}c^2 + B_{13}ac\cos\beta)$.

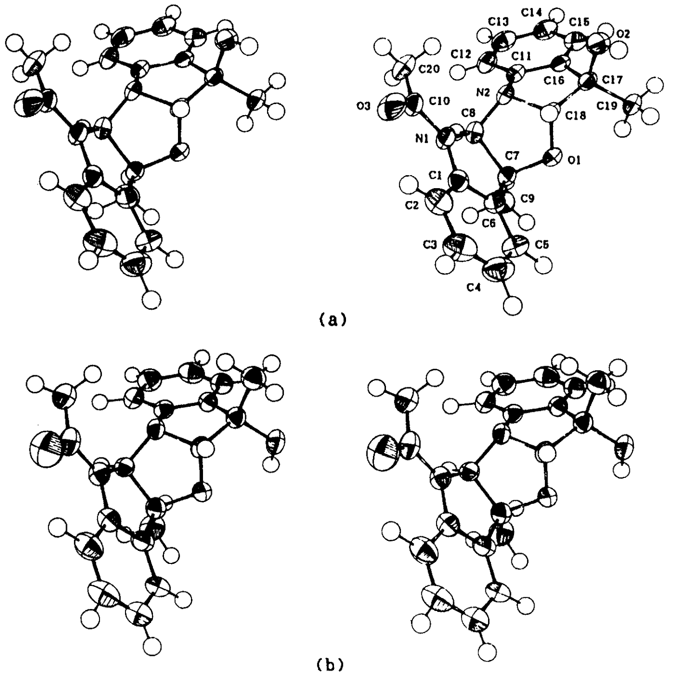


Fig. 1. Stereoscopic Drawings of the Molecular Structures of **1b** (a) and **2b** (b)

The bond lengths and bond angles for **1b**, and selected torsional angles in the five-membered rings for **1b** as well as **2b** are listed in Tables II and III, respectively. The bond lengths in **1b** are almost the same as those found in **2b** within the experimental error; the averaged and maximum differences in the corresponding lengths between **1b** and **2b** are 0.009(8) Å and 0.027(6) Å.[7] The bond angles in the skeletons of both molecules are also similar; the averaged and maximum differences in the corresponding angles between **1b** and **2b** are 0.8(6)° and 2.6(4)°. But some differences in the bond angles between **1b** and **2b** are found around the C(17) atom; *e.g.*, the O(2)–C(17)–C(19) angles are 111.2(3)° (**1b**) and 106.7(3)° (**2b**). The only significant difference between **1b** and **2b** is found in the torsional angles in the A and B rings. The torsional angles in the A ring of **1b** are smaller than those of **2b**, and those in the B ring of **1b** form a typical envelope conformation set; C(18) is shifted by 0.50 Å from the plane through the other four atoms. The conformations of the A, B, and C rings in **1b** (**2b**) are nearly planar (slighly envelope), envelope (half-chair), and envelope (envelope), respectively. The dihedral angles between the least-squares planes for the A, B, and C rings are as follows: A–B, 71.6° (**1b**) and 69.7° (**2b**); A–C, 52.5° (**1b**) and 55.2° (**2b**); B–C, 60.4° (**1b**) and 64.8° (**2b**).

As mentioned above, the opposite configurations at the C_{12} position involving methyl and hydroxyl substituents cause small differences in the ring structure. The present result indicates the rigidity of the pentacyclic ring structure of 6*H*-oxazolo[3,2-*a*:4,5-*b*′]diindole.

Table II. Bond Lengths and Bond Angles for **1b** with Their Estimated Standard Deviations in Parentheses

a) Bond lengths (l/Å)

O(1)–C(7)	1.430 (4)	C(5)–C(6)	1.398 (5)
O(1)–C(18)	1.425 (4)	C(6)–C(7)	1.487 (5)
O(2)–C(17)	1.422 (4)	C(7)–C(8)	1.572 (5)
O(3)–C(10)	1.220 (5)	C(7)–C(9)	1.511 (5)
N(1)–C(1)	1.417 (4)	C(10)–C(20)	1.496 (6)
N(1)–C(8)	1.465 (4)	C(11)–C(12)	1.386 (5)
N(1)–C(10)	1.374 (4)	C(11)–C(16)	1.384 (5)
N(2)–C(8)	1.439 (4)	C(12)–C(13)	1.385 (5)
N(2)–C(11)	1.428 (4)	C(13)–C(14)	1.372 (6)
N(2)–C(18)	1.475 (4)	C(14)–C(15)	1.398 (5)
C(1)–C(2)	1.384 (5)	C(15)–C(16)	1.374 (5)
C(1)–C(6)	1.391 (5)	C(16)–C(17)	1.521 (5)
C(2)–C(3)	1.386 (6)	C(17)–C(18)	1.530 (5)
C(3)–C(4)	1.382 (6)	C(17)–C(19)	1.527 (5)
C(4)–C(5)	1.375 (6)		

b) Bond angles (θ/°)

C(7)–O(1)–C(18)	108.6 (3)	N(1)–C(8)–C(7)	105.3 (2)
C(1)–N(1)–C(8)	110.8 (3)	N(2)–C(8)–C(7)	105.1 (2)
C(1)–N(1)–C(10)	124.9 (3)	O(3)–C(10)–N(1)	121.2 (3)
C(8)–N(1)–C(10)	123.9 (3)	O(3)–C(10)–C(20)	121.7 (3)
C(8)–N(2)–C(11)	119.1 (3)	N(1)–C(10)–C(20)	117.1 (3)
C(8)–N(2)–C(18)	106.1 (2)	N(2)–C(11)–C(12)	127.7 (3)
C(11)–N(2)–C(18)	104.9 (2)	N(2)–C(11)–C(16)	111.1 (3)
N(1)–C(1)–C(2)	129.7 (3)	C(12)–C(11)–C(16)	121.1 (4)
N(1)–C(1)–C(6)	109.0 (3)	C(11)–C(12)–C(13)	117.7 (3)
C(2)–C(1)–C(6)	121.4 (4)	C(12)–C(13)–C(14)	121.8 (4)
C(1)–C(2)–C(3)	117.7 (4)	C(13)–C(14)–C(15)	119.9 (4)
C(2)–C(3)–C(4)	121.7 (4)	C(14)–C(15)–C(16)	118.8 (3)
C(3)–C(4)–C(5)	120.5 (4)	C(11)–C(16)–C(15)	120.6 (4)
C(4)–C(5)–C(6)	118.9 (3)	C(11)–C(16)–C(17)	109.5 (2)
C(1)–C(6)–C(5)	119.9 (4)	C(15)–C(16)–C(17)	129.9 (3)
C(1)–C(6)–C(7)	112.3 (3)	O(2)–C(17)–C(16)	107.3 (3)
C(5)–C(6)–C(7)	127.8 (3)	O(2)–C(17)–C(18)	108.8 (3)
O(1)–C(7)–C(6)	112.9 (3)	O(2)–C(17)–C(19)	111.2 (3)
O(1)–C(7)–C(8)	103.6 (2)	C(16)–C(17)–C(18)	101.0 (3)
O(1)–C(7)–C(9)	107.7 (2)	C(16)–C(17)–C(19)	113.9 (3)
C(6)–C(7)–C(8)	102.7 (3)	C(18)–C(17)–C(19)	113.9 (3)
C(6)–C(7)–C(9)	114.7 (3)	O(1)–C(18)–N(2)	103.9 (2)
C(8)–C(7)–C(9)	114.8 (3)	O(1)–C(18)–C(17)	112.6 (3)
N(1)–C(8)–N(2)	112.0 (2)	N(2)–C(18)–C(17)	106.6 (2)

Table III. Selected Torsional Angles (ϕ/°) for **1b** and **2b** with Their Estimated Standard Deviations in Parentheses

Atoms	**1b**	**2b**
Ring A		
C(8)–N(1)–C(1)–C(6)	−1.2 (4)	4.9 (5)
C(1)–N(1)–C(8)–C(7)	1.7 (3)	−7.6 (4)
N(1)–C(1)–C(6)–C(7)	0.2 (4)	0.1 (5)
C(1)–C(6)–C(7)–C(8)	0.8 (4)	−4.6 (5)
C(6)–C(7)–C(8)–N(1)	−1.5 (3)	7.2 (4)
Ring B		
C(18)–O(1)–C(7)–C(8)	22.5 (3)	11.3 (4)
C(7)–O(1)–C(18)–N(2)	−35.7 (3)	−27.6 (4)
C(18)–N(2)–C(8)–C(7)	−20.3 (3)	−25.3 (4)
C(8)–N(2)–C(18)–O(1)	34.4 (3)	33.0 (4)
O(1)–C(7)–C(8)–N(2)	−0.7 (3)	8.8 (4)
Ring C		
C(18)–N(2)–C(11)–C(16)	−19.5 (4)	−17.0 (4)
C(11)–N(2)–C(18)–C(17)	26.6 (3)	25.5 (4)
N(2)–C(11)–C(16)–C(17)	4.4 (4)	1.0 (5)
C(11)–C(16)–C(17)–C(18)	11.8 (4)	14.1 (5)
C(16)–C(17)–C(18)–N(2)	−23.2 (3)	−23.7 (4)

The crystal structure of **1b** is stereographically depicted in Fig. 2. The crystals of both **1b** and **2b** are built up by hydrogen-bonded rows of molecules, the hydrogen bonds, O(2)–H···O(3), being formed between molecules related by a glide plane in **1b**, and between molecules related by a glide plane and translation in **2b**.[8] The difference in crystal packing between **1b** and **2b** is due to the different direction of the hydrogen bonds. The hydroxyl group is *cis* to the acetyl group in **1b** while *trans* in **2b** (see Fig. 1). The hydrogen-bonded molecules consequently form a zigzag

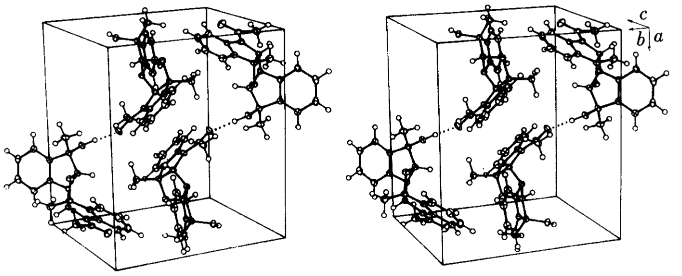


Fig. 2. Stereoscopic Drawing of the Crystal Packing of **1b**

Hydrogen bonds are indicated by dotted lines.

band along a glide plane and extend in the direction of the *a* axis in **1b**.

References and Notes

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7) The estimated standard deviation (E.S.D.) for the difference in the corresponding bond lengths (angles) is taken to be $(\sigma_1^2+\sigma_2^2)^{1/2}$, where σ_1 and σ_2 are E.S.D.'s for individual parameters. The E.S.D. for the mean value of the differences is taken to be $[\Sigma(d_i-d_m)^2/(n-1)]^{1/2}$, where d_i and d_m are the *i*th value in a set of *n* such values and the arithmetic mean of the *n* values, respectively.
8) The hydrogen-bond parameters are as follows.
1b: $O(2)(x, y, z) \cdots O(3)(0.5+x, 0.5-y, z) = 2.822(4)$ Å.
2b: $O(2)(x, y, z) \cdots O(3)(-0.5+x, 0.5-y, -1+z) = 2.796(4)$ Å.