Table 3. *Selected geometric parameters (Å, °) for (2)*

C9—H9	0.95 (2)	C2′—C1′	1.407 (3)
C9—C8a	1.530 (3)	C2′—C7′	1.548 (3)
C9—C9a	1.525 (3)	C2′—C3′	1.402 (3)
C9—C1′	1.528 (3)		
H9—C9—C8a	107.7 (14)	C1′—C2′—C7′	123.7 (2)
H9—C9—C9a	108.0 (15)	C3′—C2′—C7′	119.9 (2)
H9—C9—C1′	109.1 (14)		
C1—C9a—C9—C1′	−50.3 (3)	C1—C9a—C9—C8a	−175.5 (2)
C1—C9a—C9—H9	71.3 (14)	C8—C8a—C9—C9a	176.8 (2)
C4′—C3′—C2′—C7′	−178.4 (2)	H9—C9—C1′—C2′	3.3 (14)
C6′—C1′—C2′—C7′	178.8 (2)	H9—C9—C1′—C6′	−176.1 (14)

In both structures, the H9 atoms were refined isotropically. All other H atoms were riding.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995); program(s) used to solve structures: *TEXSAN SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN LS* and *SHELXL*93 (Sheldrick, 1993); molecular graphics: *TEXSAN ORTEP* (Johnson, 1965); software used to prepare material for publication: *TEXSAN*, *SHELXL*93 and *PLATON* (Spek, 1990).

Partial support of this research from Southern Illinois University through doctoral fellowship (YH) and Distinguished Professorship (CYM) funding and from the University Research Foundation (URF, La Jolla, CA, USA) is graciously acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1380). Services for accessing these data are described at the back of the journal. A displacement ellipsoid plot of molecule (1*b*) has also been deposited.

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First Determination of the Absolute Configuration of an Atropisomeric Flavin Derivative

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Abstract

The crystal structure and absolute configuration of the (−)-enantiomer of 3-(4,6-dibromo-2-methylphenyl)-10-(4-*tert*-butylphenyl)pyrimido[4,5-*b*]quinoline-2,4(3*H*,10*H*)-dione methanol solvate, $C_{28}H_{23}Br_2N_3O_2.CH_4O$, have been determined. The absolute configuration is *S*. The asymmetric unit contains two crystallographically independent molecules which are related by a pseudo-inversion center.

Comment

In the course of studies to determine precisely the reaction mechanism of flavoenzyme (Walsh, 1979), various optically active 5-deazaflavin derivatives have been synthesized and their stereochemical reactivities have been investigated in detail (Tanaka *et al*, 1987; Shinkai, Kawase *et al.*, 1989; Shinkai, Yamaguchi *et al.*, 1989; Kawamoto *et al.*, 1989, 1990, 1992, 1992*a*,*b*, 1994; Ohno *et al.*, 1994, 1996).

However, few determinations of the absolute configurations of these chiral flavoenzyme models have been achieved so far. Therefore, we synthesized the title flavin derivative, (I), and performed an X-ray crystallographic analysis of the (−)-enantiomer using the anomalous dispersion effect of the Br atoms. The asymmetric unit contains two molecules and corresponding bond lengths and angles do not differ significantly between these molecules.

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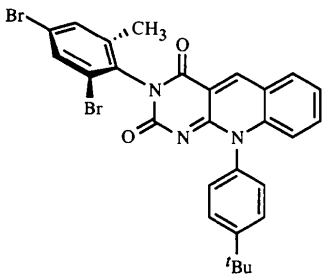

(*S*)-(−)-(I)

The pyrimidoquinoline rings are nearly planar, *i.e.* to within 0.126 (4) Å in molecule *A* and 0.134 Å in molecule *B*. The compound has an axial chirality with respect to the orientation of the dibromo-2-methylphenyl ring. The principal differences between the two molecules are in the dihedral angles between the aromatic rings. The dihedral angle between the pyrimidoquinoline and dibromo-2-methylphenyl rings are 113.2 and 66.4° in molecules *A* and *B*, respectively, and those between the pyrimidoquinoline and *p-tert*-butylphenyl rings are 96.6 and 98.5° in molecules *A* and *B*, respectively.

Full-matrix least-squares refinements using anomalous dispersion factors for all non-H atoms resulted in an *R* factor of 0.034 for the present structure and 0.054 for the other enantiomorph. Consequently the absolute configuration of (−)-(I) has been assigned to be *S*. The Flack parameter (Flack, 1983) also confirmed this assignment. There is a hydrogen bond between N1 of (I) and the hydroxyl group (O3—H24) of the methanol of crystallization.

This determination of the absolute configuration of chiral (I) is useful for future studies in bioorganic chemistry because it allows elucidation of the absolute configuration of the analog on debromination of compound (I) (Ohno *et al.*, 1996) and the CD spectrum of the debrominated compound can be used as a reliable basis for the conformational assignments of all 5-deazaflavin derivatives reported previously (Kawamoto *et al.*, 1992*a*,*b*).

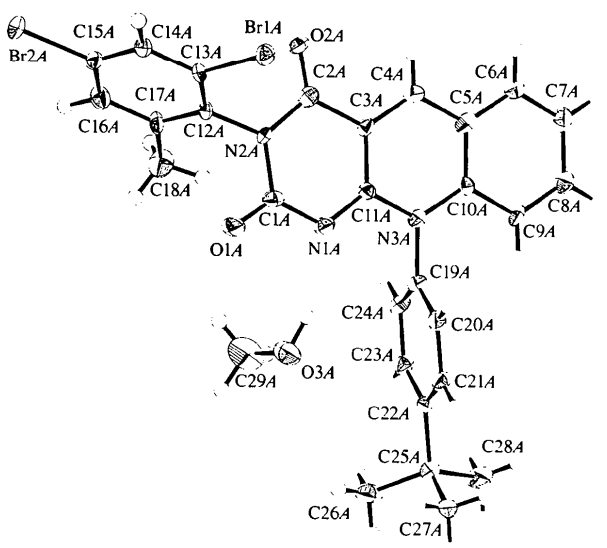

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of molecule *A* of (I) showing displacement ellipsoids at the 50% probability level.

Experimental

The synthesis of (I) was carried out as reported previously (Ohno *et al.*, 1994) starting from 4,6-dibromo-*o*-toluidine, which was prepared by bromination of *o*-toluidine. The optical resolution was accomplished by HPLC [column, Chiralcel OD; eluent, ethanol; flow rate, 1.5 ml min^{-1}; detection, UV 254 nm; retention times, 89.5 min for (+)- and 95.6 min for (−)-enantiomer] and both enantiomers were obtained in >99% e.e. The crystal of the (−)-enantiomer which was subjected to X-ray crystallographic analysis was obtained by recrystallization from methanol at room temperature.

Crystal data

$C_{28}H_{23}Br_2N_3O_2.CH_4O$
M_r = 625.36
Monoclinic
$P2_1$
a = 20.913 (7) Å
b = 10.868 (8) Å
c = 12.03 (1) Å
β = 100.45 (4)°
V = 2687 (2) Å^3
Z = 4
D_x = 1.545 Mg m^{-3}
D_m = 1.51 Mg m^{-3}
D_m measured by flotation in C_6H_{14}/CCl_4
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 24 reflections
θ = 14.9–15.1°
μ = 3.061 mm^{-1}
T = 173.2 K
Prismatic
0.4 × 0.4 × 0.2 mm
Yellow

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.440, T_{max} = 0.542
9752 measured reflections
9469 independent reflections
8524 reflections with $I > 1.5\sigma(I)$
R_{int} = 0.045
θ_{max} = 25.02°
h = −24 → 0
k = −12 → 12
l = −14 → 14
3 standard reflections
every 150 reflections
intensity decay: 0.17%

Refinement

Refinement on F
R = 0.034
wR = 0.052
S = 0.862
8524 reflections
667 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o) + 0.0025|F_o|^2]$
$(\Delta/\sigma)_{max}$ = 0.0204
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 0.0002 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.021 (1)

Table 1. *Selected geometric parameters (Å, °)*

N1*A*—C1*A*	1.378 (7)	N3*A*—C11*A*	1.382 (6)
N1*A*—C11*A*	1.314 (6)	N3*A*—C19*A*	1.451 (6)
N2*A*—C1*A*	1.435 (6)	C2*A*—C3*A*	1.489 (7)
N2*A*—C2*A*	1.379 (6)	C3*A*—C4*A*	1.368 (7)
N2*A*—C12*A*	1.445 (6)	C3*A*—C11*A*	1.429 (6)
N3*A*—C10*A*	1.389 (6)	C4*A*—C5*A*	1.418 (7)
C1*A*—N1*A*—C11*A*	118.4 (4)	C2*A*—C3*A*—C11*A*	117.6 (4)
C1*A*—N2*A*—C2*A*	123.9 (4)	C3*A*—C4*A*—C5*A*	120.6 (4)
C1*A*—N2*A*—C12*A*	118.4 (4)	C4*A*—C5*A*—C10*A*	117.7 (4)
C10*A*—N3*A*—C11*A*	122.5 (4)	N3*A*—C10*A*—C5*A*	120.4 (4)
C11*A*—N3*A*—C19*A*	119.2 (4)	N1*A*—C11*A*—N3*A*	118.1 (4)
N1*A*—C1*A*—N2*A*	119.5 (4)	N1*A*—C11*A*—C3*A*	125.2 (4)
N2*A*—C2*A*—C3*A*	114.2 (4)	N3*A*—C11*A*—C3*A*	116.7 (4)
C2*A*—C3*A*—C4*A*	120.3 (4)		

The space group was uniquely determined from the systematic absence: $0k0$ when $k = 2n + 1$. Bijvoet pairs were not averaged. The non-H atoms were refined anisotropically and H atoms were placed in calculated positions but not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: direct methods *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1036). Services for accessing these data are described at the back of the journal.

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3-[(Z)-Piperidin-1-ylmethylidene]-2,3-dihydro-1,4-benzodioxan-2-one

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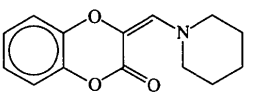
Abstract

The crystal structure of the title compound has been determined in order to obtain the geometry of one isomer of $C_{14}H_{15}NO_3$. The molecule has the unusual feature of a planar dioxane ring and several bond angles are enlarged due to steric hindrance.

Comment

In connection with our investigations into 1,4-benzodioxane chemistry, the reaction between 1,4-benzodioxane-2-carboxylic acid and some amines has been studied (Ruiz *et al.*, 1996), and the title compound, (I), was isolated. Although spectroscopic data show that (I) is clearly different from its isomer 2-piperidinylcarbonyl-1,4-benzodioxane, X-ray diffraction analysis has permitted the determination of the structure and geometry of this new unexpected compound.



(I)