1648 measured reflections
1460 independent reflections
839 reflections with $I > 2\sigma(I)$
3 standard reflections every 100 reflections
intensity decay: −1.6%

Refinement

Refinement on F^2
$R(F) = 0.034$
$wR(F^2) = 0.082$
$S = 1.086$
1460 reflections
115 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 0.1415P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.165$ e Å^{-3}
$\Delta\rho_{\min} = -0.148$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.038 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—B1	1.357 (3)	N3—C4	1.291 (3)
N2—N3	1.371 (2)	C4—C4a	1.437 (3)
N2—B1	1.433 (3)	C4a—C8a	1.404 (3)
N2—C2	1.457 (3)	C8a—B1	1.539 (3)
B1—O1—H1	118.1 (18)	C8a—C4a—C4	118.4 (2)
N3—N2—B1	124.4 (2)	C8—C8a—B1	125.8 (2)
N3—N2—C2	112.0 (2)	C4a—C8a—B1	117.0 (2)
B1—N2—C2	123.6 (2)	O1—B1—N2	116.3 (2)
C4—N3—N2	118.1 (2)	O1—B1—C8a	128.2 (2)
N3—C4—C4a	126.6 (2)	N2—B1—C8a	115.5 (2)
B1—N2—N3—C4	−0.4 (3)	C2—N2—B1—O1	−1.8 (3)
C2—N2—N3—C4	178.8 (2)	N3—N2—B1—C8a	−1.3 (3)
N2—N3—C4—C4a	1.4 (3)	C2—N2—B1—C8a	179.7 (2)
N3—C4—C4a—C8a	−0.6 (3)	C4a—C8a—B1—O1	−176.4 (2)
C4—C4a—C8a—B1	−1.2 (3)	C4a—C8a—B1—N2	2.0 (3)
N3—N2—B1—O1	177.3 (2)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N3^{i}	0.82 (3)	2.02 (3)	2.810 (2)	161 (3)

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

The H1 atom was refined isotropically. All other H atoms are riding.

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 structure: *TEXSAN SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *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).

This work was supported by grant GM44819 from the National Institutes of Health. We thank Mr Lin Yi for conducting the first preparation of (3) in our laboratory.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1385). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 73–77

Exclusivity of the *sp* Rotamers of 9-(*o-tert*-Butylphenyl)fluorene and 9-(*o-tert*-Butylphenyl)-9-fluorenol in Solution and the Crystalline State

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Abstract

Both 9-(*o-tert*-butylphenyl)fluorene ($C_{23}H_{22}$) and 9-(*o-tert*-butylphenyl)-9-fluorenol ($C_{23}H_{22}O$) maintained *sp* rotameric structures exclusively in crystalline form as well as in solution. This result is in contrast to that

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obtained for the corresponding 9-(*o*-isopropylphenyl)-fluorene and 9-(*o*-isopropylphenyl)-9-fluorenol. In-plane sterically imposed distortion of the *tert*-butyl group is exhibited in *sp*-9-(*o*-*tert*-butylphenyl)fluorene and to a much larger extent in *sp*-9-(*o*-*tert*-butylphenyl)-9-fluorenol. The asymmetric unit of the latter contains two crystallographically distinct, but nearly identical, molecules which are hydrogen bonded to each other *via* their respective OH groups; hydrogen bonding between the crystallographically equivalent molecules is not observed.

Comment

Of the two rotameric structures that may arise with 9-substituted fluorenes, it is difficult to predict which will be present in solution and which in the crystalline form. Some examples are given in Fig. 1. We have observed that 9-pivaloylfluorene exists only as its *ap* rotamer in solution and in the crystalline form (Meyers *et al.*, 1991). In contrast, the *sp* rotamer of 9-pivaloyl-9-fluorenol is the exclusive structure in both states (Meyers *et al.*, 1992). And, while *ap*- and *sp*-*Z*-9-pivaloylfluorene oxime coexist in solution, the crystalline form consists solely of the *ap* rotamer (Robinson *et al.*, 1994). In earlier work, Nakamura *et al.* (1977*a*) (see also Ōki, 1993) found that *ap*- and *sp*-9-(*o*-isopropylphenyl)fluorene exist as an equilibrating mixture in solution. We verified this result but also found that the *sp* rotamer alone constitutes the crystalline form (Meyers, Hou, Scott & Robinson, 1997; Meyers, Hou, Scott, Robinson *et al.*, 1997). In contrast, the *ap* rotamer of 9-(*o*-isopropylphenyl)-9-fluorenol is the exclusive structure in solution (Nakamura *et al.*, 1977*a*) and crystalline form (Meyers, Hou, Scott, Robinson *et al.*, 1997).

These examples illustrate that rotamer preference of these rotationally hindered 9-substituted fluorenes in solution is largely determined by their relative intrinsic rotational barriers, while in the crystalline form, the preference can be significantly influenced by the relative stabilities of their molecular packing. On this basis, we reasoned that the *sp* conformation of 9-(*o*-*tert*-butylphenyl)-9-fluorenol, (1), and 9-(*o*-*tert*-butylphenyl)fluorene, (2), shown by ^{1}H NMR to be the exclusive or almost exclusive structures in solution (Nakamura *et al.*, 1977*b*; Meyers *et al.*, 1995; Meyers, Hou, Lutfi *et al.*, 1997) might not represent these molecules in their crystalline form. For this reason, we undertook the study of their X-ray structures. The preparation of (1) and (2) is shown in Fig. 1.

It was immediately ascertained that crystalline (1) and (2) are *sp* rotamers, just as they are in solution.

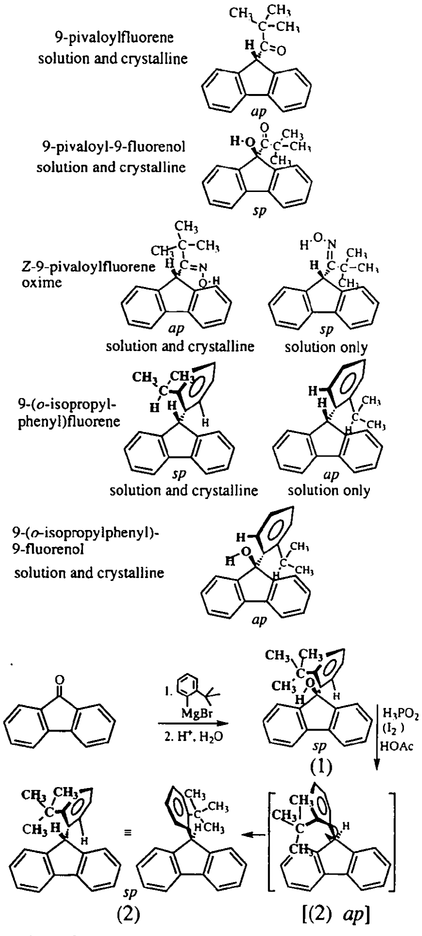

Fig. 1. Examples of rotamers of some hindered 9-substituted fluorenes in solution and the crystalline form, and the preparation of compounds (1) and (2).

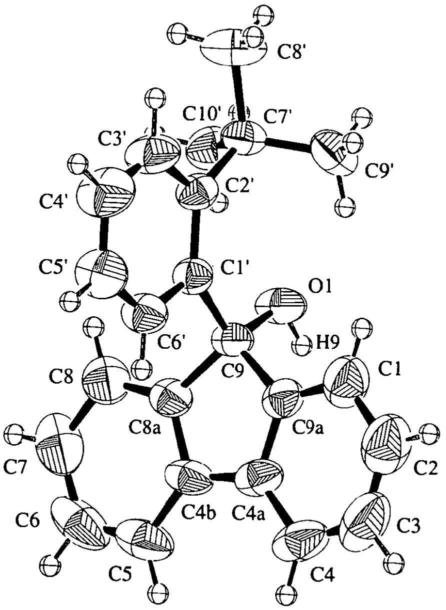

Fig. 2. The molecular structure and atom-numbering scheme for (1*a*) with displacement ellipsoids at the 50% probability level.

Unexpectedly, the structure of compound (1) was found to be composed of two crystallographically distinct, but very similar, molecules, (1*a*) and (1*b*). The crystal structure of (1*a*) with atom numbering is shown in Fig. 2 and that of (2) is shown in Fig. 3. An *ORTEP* (Johnson, 1965) drawing of (1*b*) has been deposited with the supplementary material; the atom numbering is identical to that of (1*a*), but has an *X* appended to each atom label. Selected comparative geometric parameters are provided in Tables 1 and 3.

Structures (1*a*) and (1*b*) differ from each other in certain geometric features. The asymmetric unit is composed of a (1*a*)–(1*b*) pair in which (1*a*) is hydrogen bonded to (1*b*) through their respective OH groups, that of (1*a*) being the donor and that of (1*b*) being the acceptor (Table 2 and Fig. 4). There is no hydrogen bonding between crystallographically equivalent molecules. The differences between corresponding torsion angles, 59 (7)° between H9—O1—C9—C1′ in (1*a*) and H9*X*—O1*X*—C9*X*—C1′*X* in (1*b*), 7.4 (6)° between C1—C9a—C9—C1′ in (1*a*) and C1*X*—C9a*X*—C9*X*—C1′*X* in (1*b*), and 5.1 (6)° between C1—C9a—C9—O1 in (1*a*) and C1*X*—C9a*X*—C9*X*—O1*X* in (1*b*), are substantially larger than any other differences between (1*a*) and (1*b*). It is reasonable to believe that stabilization of the molecular packing is attained *via* the intermolecular hydrogen bonding which, because of the large steric effects, is best enabled between structures (1*a*) and (1*b*). The large in-plane distortion of the *tert*-butyl group imposed by O1 is manifested in the much larger angle of C1′—C2′—C7′ compared with C3′—C2′—C7′ in (1*a*) by 9.9 (4)°, and of C1′*X*—C2′*X*—C7′*X* compared with C3′*X*—C2′*X*—C7′*X* in (1*b*) by 10.7 (5)°. The phenyl and fluorene planes are essentially perpendicular in (1*a*) and (1*b*).

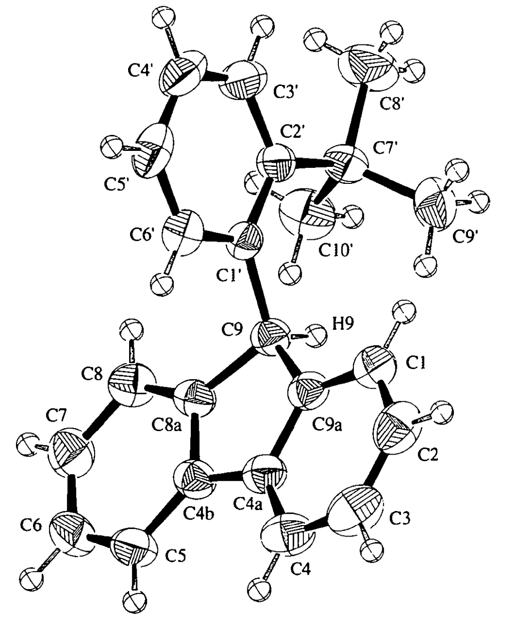

Fig. 3. The molecular structure and atom-numbering scheme for (2) with displacement ellipsoids at the 50% probability level.

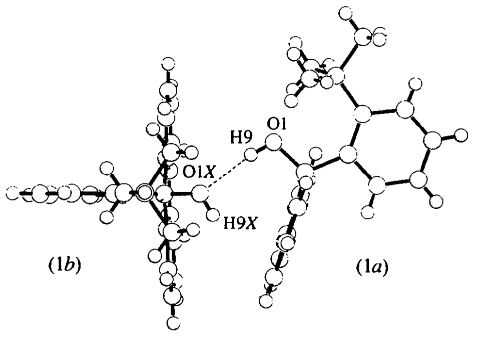

Fig. 4. Hydrogen bonding between the two crystallographically distinct molecules (1*a*) and (1*b*).

Unlike (1), crystalline (2) exhibits no hydrogen bonding and its asymmetric unit contains a single molecule. In-plane distortion of the *tert*-butyl group sterically imposed by H9 in (2) is much less significant than that imposed by O1 in (1); in (2), angle C1′—C2′—C7′ is larger than C3′—C2′—C7′ by only 3.8 (4)°. This difference in steric effect is also apparent from the substantially smaller angle of H9—C9—C1′ in (2) compared with the corresponding angle O1—C9—C1′ in (1*a*) and (1*b*), and of C1—C9a—C9—C1′ in (2) compared with the same angle in (1*a*) and (1*b*), and from the larger angle of C1—C9a—C9—H9 in (2) compared with the corresponding angle C1—C9a—C9—O1 in (1*a*) and (1*b*). As in (1*a*) and (1*b*), the phenyl and fluorene planes of (2) are essentially perpendicular.

These results clearly demonstrate that regardless of the strain imparted to (1) and (2) in their *sp* structures by the bulky *o*-*tert*-butyl group, the substantially greater strain associated with their *ap* structures precludes the latter from existing in solution or crystalline form.

Experimental

sp-9-(*o*-*tert*-Butylphenyl)-9-fluorenol, (1), was prepared by the reaction of *o*-*tert*-butylphenylmagnesium bromide with fluorenone [76% yield, 97% conversion based on unrecovered fluorenone; colorless crystals (from isooctane), m.p. 431–432 K (corr.), used for the X-ray study] following the procedure of Nakamura *et al.* (1977*b*), who reported m.p. 429.5–431 K. ^{1}H NMR (Varian VXR 300, $CDCl_3$), δ: 1.81 (*s*, 9H), 2.35 (*s*, 1H), 6.42 (*dd*, *J* = 7.8, 1.5 Hz, 1H), 6.75 (*ddd*, *J* = 1.2, 7.65, 7.8 Hz, 1H), 7.05 (*ddd*, *J* = 8.10, 7.65, 1.5 Hz, 1H), 7.19–7.26 (*ddd*, *J* = 1.2 Hz, 2H), 7.28–7.38 (*m*, 4H), 7.57 (*dd*, *J* = 8.1, 1.2 Hz, 1H), 7.67 (*dd*, *J* = 7.5, 0.9 Hz, 2H). *sp*-9-(*o*-*tert*-Butylphenyl)fluorene, (2), was formed quantitatively from (1) refluxed in acetic acid with a tenfold molar amount of 50% aqueous H_3PO_2 (*d* = 1.274) for 30 min [white crystals from a mixture of hexanes–isooctane, m.p. 452–453 K (corr.), were used for the X-ray study]. The presence of varying amounts of I_2 in the refluxing mixture did not alter the results. Using HI in acetic acid for this conversion, Nakamura *et al.* (1977*b*) reported m.p. 452.5–453.5 K. ^{1}H NMR (Varian VXR 500, $CDCl_3$), δ: 1.72 (*s*, 9H), 5.86 (*s*, 1H), 6.22 (*dd*, J = 7.75, 1.55 Hz, 1H), 6.87 (*ddd*, J = 1.30, 7.45, 7.45 Hz, 1H), 7.11 (*ddd*, J = 8.10, 7.65, 1.55 Hz, 1H), 7.21–7.25 (*m*, 4H), 7.38 (*m*, 2H), 7.49 (*dd*, J = 8.15, 1.30 Hz, 1H), 7.80–7.84 (*d*, J = 7.6 Hz, 2H). ^{13}C NMR (Varian VXR 300, 75 MHz for ^{13}C, $CDCl_3$), δ: 32.60, 35.65, 51.02, 119.84, 125.17, 125.77, 126.29, 126.43, 127.05, 127.39, 130.9, 139.97, 141.11, 148.19, 150.01.

Compound (1)

Crystal data

$C_{23}H_{22}O$
$M_r = 314.43$
Monoclinic
$P2_1/c$
$a = 15.865\,(4)$ Å
$b = 11.886\,(6)$ Å
$c = 20.252\,(4)$ Å
$\beta = 112.438\,(14)^\circ$
$V = 3530\,(2)$ Å^3
$Z = 8$
$D_x = 1.183$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10.10$–10.43°
$\mu = 0.070$ mm^{-1}
$T = 296$ K
Irregular fragment
0.44 × 0.41 × 0.27 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (rate 3° min^{-1} in ω)
Absorption correction: none
6364 measured reflections
6122 independent reflections
2879 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.013$
$\theta_{\max} = 25^\circ$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 14$
$l = -24 \rightarrow 22$
3 standard reflections every 100 reflections intensity decay: 1.1%

Refinement

Refinement on F^2
$R(F) = 0.042$
$wR(F^2) = 0.107$
$S = 1.111$
6118 reflections
447 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 0.4512P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.144$ e Å^{-3}
$\Delta\rho_{\min} = -0.178$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C9	1.428 (3)	O1*X*—C9*X*	1.440 (3)
C8a—C9	1.529 (3)	C8a*X*—C9*X*	1.515 (4)
C9—C9a	1.532 (3)	C9*X*—C9a*X*	1.533 (4)
C1′—C9	1.540 (3)	C1′*X*—C9*X*	1.553 (3)
C1′—C2′	1.417 (3)	C1′*X*—C2′*X*	1.417 (3)
C2′—C7′	1.552 (3)	C2′*X*—C7′*X*	1.543 (4)
C2′—C3′	1.404 (4)	C2′*X*—C3′*X*	1.401 (4)
O1—C9—C8a	109.0 (2)	O1*X*—C9*X*—C8a*X*	108.1 (2)
O1—C9—C9a	109.1 (2)	O1*X*—C9*X*—C9a*X*	108.8 (2)
O1—C9—C1′	113.5 (2)	O1*X*—C9*X*—C1′*X*	115.1 (2)
C1′—C2′—C7′	127.3 (2)	C1′*X*—C2′*X*—C7′*X*	127.3 (2)
C3′—C2′—C7′	117.4 (2)	C3′*X*—C2′*X*—C7′*X*	116.6 (3)
C1—C9a—C9—C1′	−57.1 (3)		
C1—C9a—C9—O1	69.0 (3)		
C7′—C2′—C3′—C4′	177.9 (3)		
C6′—C1′—C2′—C7′	−177.9 (2)		
C8a—C9—C9a—C1	−176.3 (3)		
C8—C8a—C9—C9a	176.6 (3)		
C2′—C1′—C9—O1	−2.0 (4)		
C6′—C1′—C9—O1	178.2 (2)		
H9—O1—C9—C1′	177 (2)		
C1*X*—C9a*X*—C9*X*—C1′*X*	−64.5 (3)		
C1*X*—C9a*X*—C9*X*—O1*X*	63.9 (3)		
C7′*X*—C2′*X*—C3′*X*—C4′*X*	179.6 (2)		
C6′*X*—C1′*X*—C2′*X*—C7′*X*	−179.9 (2)		
C8a*X*—C9*X*—C9a*X*—C1*X*	177.5 (3)		
C8*X*—C8a*X*—C9*X*—C9a*X*	−178.6 (3)		
C2′*X*—C1′*X*—C9*X*—O1*X*	1.7 (4)		
C6′*X*—C1′*X*—C9*X*—O1*X*	−179.9 (2)		
H9*X*—O1*X*—C9*X*—C1′*X*	118 (5)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H9···O1*X*	0.86 (3)	2.10 (3)	2.953 (3)	171 (3)

Compound (2)

Crystal data

$C_{23}H_{22}$
$M_r = 298.43$
Orthorhombic
$P2_12_12_1$
$a = 10.7211\,(11)$ Å
$b = 15.186\,(2)$ Å
$c = 10.4816\,(8)$ Å
$V = 1706.5\,(3)$ Å^3
$Z = 4$
$D_x = 1.162$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 12.84$–13.71°
$\mu = 0.065$ mm^{-1}
$T = 296$ K
Block
0.43 × 0.38 × 0.35 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans (rate 4° min^{-1} in ω)
Absorption correction: none
3351 measured reflections
2817 independent reflections
1560 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.016$
$\theta_{\max} = 30.04^\circ$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 21$
$l = -2 \rightarrow 14$
3 standard reflections every 150 reflections intensity decay: 0.20%

Refinement

Refinement on F^2
$R(F) = 0.038$
$wR(F^2) = 0.096$
$S = 1.090$
2817 reflections
216 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.1746P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.166$ e Å^{-3}
$\Delta\rho_{\min} = -0.149$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0062 (17)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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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