1992). Data reduction: *Xtal*3.2 *REFCAL LSABS SORTRF*. Program(s) used to solve structure: *MULTAN*87 (Main *et al.*, 1987). Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2 *ORTEP*. Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: PA1244). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Novel Function of an Atropisomeric Flavin Model as a Host Compound

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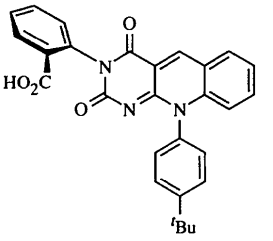
Abstract

2-[10-(4-*tert*-Butylphenyl)-2,4(3*H*,10*H*)-dioxopyrimido[4,5-*b*]quinolin-3-yl]benzoic acid methanol solvate forms a crystalline 1:1 host–guest inclusion complex with methanol, $C_{28}H_{23}N_3O_4.CH_3OH$, through a hydrogen-bonding network.

Comment

We have synthesized several atropisomeric flavoenzyme models in order to investigate the stereochemical reactivities of these compounds (Ohno *et al.*, 1994, 1996). In the course of our studies, we have also carried out X-ray crystallographic analyses of some of these compounds both for determination of absolute configuration (Kawai, Kunitomo & Ohno, 1997) and for structural interest in compounds with axial chirality (Ohno *et al.*, 1994; Ohno, Kunitomo & Kawai, 1997), and found that the title compound, 2-[10-(4-*tert*-butylphenyl)-3-(2-carboxyphenyl)pyrimido[4,5-*b*]quinoline-2,4(3*H*,10*H*)-dione, (I), affords a crystalline inclusion complex with methanol through hydrogen bonding.



(I)

An *ORTEP*II (Johnson, 1976) drawing and a stereoview of the 1:1 inclusion complex of (I) with methanol are given in Figs. 1 and 2, respectively. They show that hydrogen bonds exist between the hydroxyl group of the carboxyl group and the O atom of methanol (O4—H10···O5), as well as between the hydroxyl group of methanol and the carbonyl group of the flavin skeleton (O5—H27···O1). The same enantiomers of (I) are linked through this hydrogen-bonding network (Fig. 2).

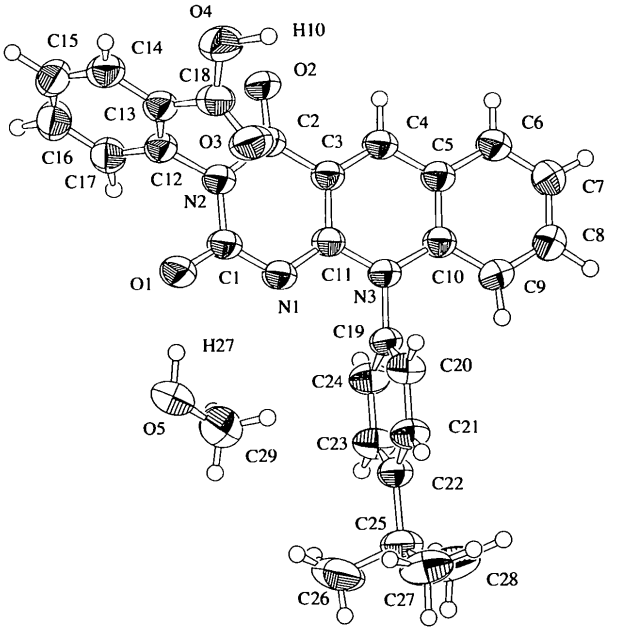


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I).CH_3OH showing displacement ellipsoids at the 50% probability level.

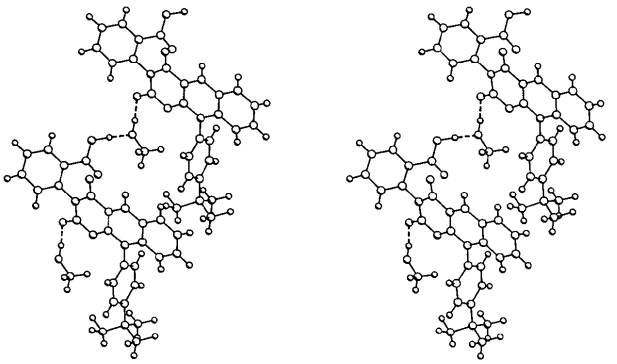


Fig. 2. Stereoview of the inclusion complex of (I).CH_3OH with methanol showing two characteristic hydrogen bonds (indicated by broken lines). Only the *R* enantiomers are illustrated here.

This result suggests that (I) has an ability to include guest molecules through a tight hydrogen-bonging network. This type of crystalline host–guest inclusion complex is attracting increasing attention from the standpoint of molecular recognition (Atwood, Davies & MacNicol, 1984; Weber, 1987, 1988), and chiral recognition of racemic guest molecules might be possible by the use of optically pure (I).

Experimental

The synthesis of (I) has been reported previously (Ohno *et al.*, 1996). The crystal used for X-ray crystallographic analysis was obtained by recrystallization from methanol at room temperature.

Crystal data

$C_{28}H_{23}N_3O_4.CH_4O$
M_r = 497.55
Monoclinic
$P2_1/n$
a = 13.613 (1) Å
b = 21.448 (3) Å
c = 9.1157 (8) Å
β = 103.561 (7)°
V = 2587.4 (5) Å^3
Z = 4
D_x = 1.277 Mg m^{-3}
D_m = 1.28 Mg m^{-3}
D_m measured by flotation in C_6H_{14}/CCl_4

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 37.2–40.0°
μ = 0.722 mm^{-1}
T = 293 K
Prismatic
0.45 × 0.40 × 0.35 mm
Yellow

Data collection

Rigaku AFC-7*R* diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.715, T_{max} = 0.777
4169 measured reflections
3990 independent reflections
3125 reflections with $I > 3\sigma(I)$
R_{int} = 0.012
θ_{max} = 60°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 24$
$l = -10 \rightarrow 9$
3 standard reflections
every 150 reflections
intensity decay: 5.91%

Refinement

Refinement on F
R = 0.0414
wR = 0.0682
S = 1.786
3125 reflections
443 parameters
All H atoms refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max}$ = 0.0240
$\Delta\rho_{max}$ = 0.259 e Å^{-3}
$\Delta\rho_{min}$ = −0.189 e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 19.872
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—C1	1.226 (2)	N3—C11	1.378 (2)
O2—C2	1.217 (2)	N3—C19	1.454 (2)
O3—C18	1.203 (2)	C2—C3	1.461 (2)
O4—C18	1.311 (2)	C3—C4	1.351 (3)
O5—C29	1.416 (3)	C3—C11	1.428 (2)
N1—C1	1.359 (2)	C4—C5	1.411 (3)
N1—C11	1.317 (2)	C5—C6	1.405 (3)
N2—C1	1.408 (2)	C5—C10	1.413 (2)
N2—C2	1.383 (2)	C6—C7	1.364 (3)
N2—C12	1.456 (2)	C7—C8	1.390 (3)
N3—C10	1.390 (2)	C8—C9	1.370 (3)
C1—N1—C11	118.4 (1)	C4—C5—C6	122.3 (2)
C1—N2—C2	123.6 (1)	C4—C5—C10	118.2 (2)
C1—N2—C12	119.0 (1)	C6—C5—C10	119.6 (2)
C2—N2—C12	117.0 (1)	C5—C6—C7	120.3 (2)
C10—N3—C11	122.4 (1)	C6—C7—C8	120.0 (2)
C10—N3—C19	119.0 (1)	C7—C8—C9	121.3 (2)
C11—N3—C19	118.6 (1)	C8—C9—C10	119.9 (2)
O1—C1—N1	122.1 (2)	N3—C10—C5	119.6 (1)
O1—C1—N2	117.3 (2)	N3—C10—C9	121.4 (2)
N1—C1—N2	120.6 (2)	C5—C10—C9	119.0 (2)
O2—C2—N2	121.8 (2)	N1—C11—N3	118.0 (1)
O2—C2—C3	123.4 (2)	N1—C11—C3	124.8 (2)
N2—C2—C3	114.8 (1)	N3—C11—C3	117.2 (1)
C2—C3—C4	120.8 (2)	O3—C18—O4	123.5 (2)
C2—C3—C11	117.7 (1)	O3—C18—C13	123.3 (2)
C4—C3—C11	121.5 (2)	O4—C18—C13	113.2 (2)
C3—C4—C5	121.1 (2)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *LS* in *TEXSAN*. Software used to prepare material for publication: *FINISH* in *TEXSAN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DE1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Configurations of Cycloadducts Formed in Asymmetric Intramolecular Diels–Alder Reactions

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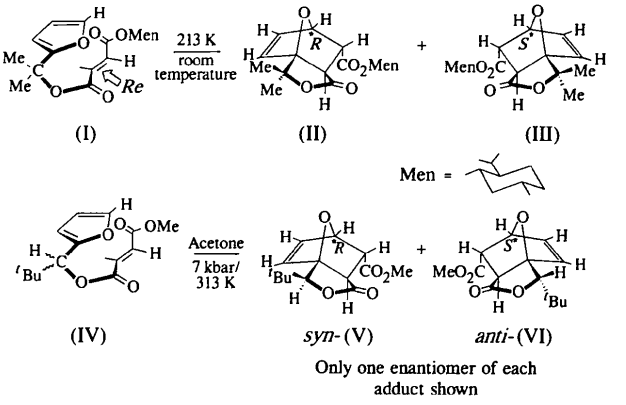
Abstract

Intramolecular cycloaddition reactions of two furfuryl fumarates yield, after crystallization, pure diastereomers of oxabicyclo[2.2.1]heptene derivatives which are versatile starting points for the total synthesis of natural products. The crystal structures of the adducts, menthyl (3a*S*,6*R*,7*R*,7a*R*)-1,3,3a,6,7,7a-hexahydro-3,3-dimethyl-1-oxo-3a,6-epoxyisobenzofuran-7-carboxylate, $C_{21}H_{30}O_5$, and methyl *syn*-3-*tert*-butyl-1,3,3a,6,7,7a-hexahydro-1-oxo-3a,6-epoxyisobenzofuran-7-carboxylate, $C_{14}H_{18}O_5$, establish the configuration at the chiral centers and provide insights into the factors controlling the diastereomeric differentiation.

Comment

Intramolecular Diels–Alder (IMDA) reactions have been shown to be of great value in the synthesis of bicyclic and polycyclic carbocycles and heterocycles (Jalis, 1984; Taber, 1984). As part of our investigations of asymmetric induction in the IMDA reactions of furan derivatives, we have determined the structures of two adducts. Menthyl (3a*S*,6*R*,7*R*,7a*R*)-1,3,3a,6,7,7a-hexahydro-3,3-dimethyl-1-oxo-3a,6-epoxyisobenzofuran-7-carboxylate, (II), could be isolated in the enantiopure form from the kinetically controlled cycloaddition of the *in situ* prepared 1-(2-furyl)-1-methylethyl menthyl fumarate, (I) (Butz, 1996; Butz & Sauer, 1997). Methyl *syn*-3-*tert*-butyl-1,3,3a,6,7,7a-hexahydro-1-oxo-3a,6-epoxyisobenzofuran-7-carboxylate, (V), has been preferentially formed over the corresponding *anti* adduct, (VI), in the high-pressure-induced reaction of 1-(2-furyl)-2,2-dimethylpropyl methyl fumarate, (IV), under thermodynamic control. The thermally induced cyclization of (IV) has been described by Jung & Gervay (1991).



Only one enantiomer of each adduct shown

In the first case, we attempted to induce π-facial diastereo-differentiation by the attachment of a menthyl ester as a chiral auxiliary (Oppolzer, 1983; Paquette, 1984; Wurziger, 1984). The diastereoselectivity achieved, however, was very disappointing. The two possible diastereomers were obtained only in a 55:45 ratio (10% diastereomeric excess). Fortunately, the major isomer (II) can be isolated in pure form with just two crystallization steps and so it is available for further synthesis. The absolute configuration of the stereocenters in compound (II) have been derived from the known absolute configuration of menthol.

The observed molecular structure of (II) (Fig. 1) implies that the diene must have attacked from the *Si* side of the dienophile. The *Si* side, however, was expected to be shielded by the isopropyl group of the auxiliary if one assumes that the conformation of the ester bond is *syn* in the transition state (Helmchen, Karge & Weetman, 1986). Since in the crystal structure the isopropyl group points towards the tricyclic adduct, whereas the rest of the menthyl skeleton points away