Acta Cryst. (1994). C**50**, 137–139

Structure of Methyl 2′-Acetoxy-6′-*tert*-butyl-2-hydroxy-1,1′-binaphthalene-3-carboxylate, $C_{28}H_{26}O_5$

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(*Received* 16 *February* 1993; *accepted* 8 *June* 1993)

Abstract

An intramolecular O1—HO1···O2 hydrogen bond is observed in the crystal structure of the title compound. The dihedral angle between the two naphthalene ring systems is 86.34 (3)°. The carbonyl group of the 2′-acetoxy fragment is oriented on the opposite side of the C1′–C10′ aromatic ring plane to the C2–O2 hydroxy fragment; the C2′—O1′—C11′—O2′ torsion angle is −7.6 (3)°.

Comment

Both naphthalene ring systems are almost planar with an interplanar angle of 86.34 (3)°. The length of the internuclear C1—C1′ bond is 1.495 (2) Å, which is consistent with a lack of orbital overlap between the two aromatic systems. Strong intramolecular hydrogen bonding, HO1···O2 1.74 (3) Å, is observed, the carboxyl segment C12—O3—C11—O2 lying in the plane of the C1–C10 ring system [the torsion angle C4—C3—C11—O3 is −1.5 (3)°]. The C11′—O2′ carbonyl group of the 2′-acetoxy segment is oriented on the opposite side of the C1′–C10′ aromatic plane to the C2—O2 segment; the torsion angles C3′—C2′—O1′—C11′ and C2′—O1′—C11′—O2′ are −63.6 (2) and −7.6 (3)°, respectively.

A systematic preparative approach to unsymmetrically substituted 2,2′-dihydroxy-1,1′-binaphthalenes was published recently (Hovorka, Gunterová & Závada, 1990; Hovorka & Závada, 1991; Hovorka, Ščigel, Gunterová, Tichý & Závada, 1992) and to our knowledge no X-ray structure determination of this type of compound has been reported. The X-ray analysis of the bromobenzene solvate of the symmetrical dimethyl 2,2′-dihydroxy-1,1′-binaphthalene-3,3′-dicarboxylate allowed the determination of its absolute configuration, showing that the dextrorotatory species possesses the (*R*) configuration (Akimoto & Iitaka, 1969; Akimoto, Shiori, Iitaka & Yamada, 1968). This finding enabled the determination of the absolute configuration of some other biaryl systems by their chemical correlation (Akimoto & Yamada, 1968, 1971).

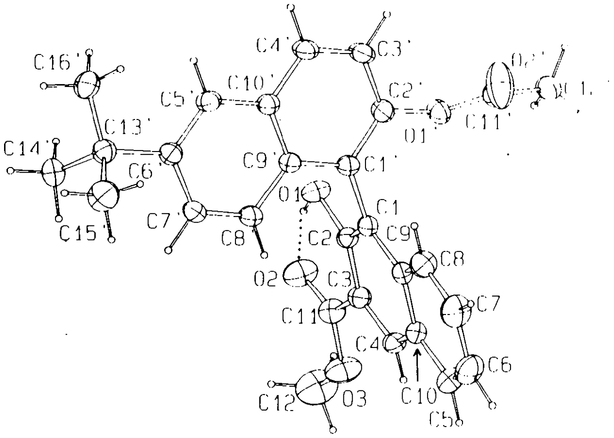

Fig. 1. View of the molecule with the atom-numbering scheme. Dashed lines indicate hydrogen bonds.

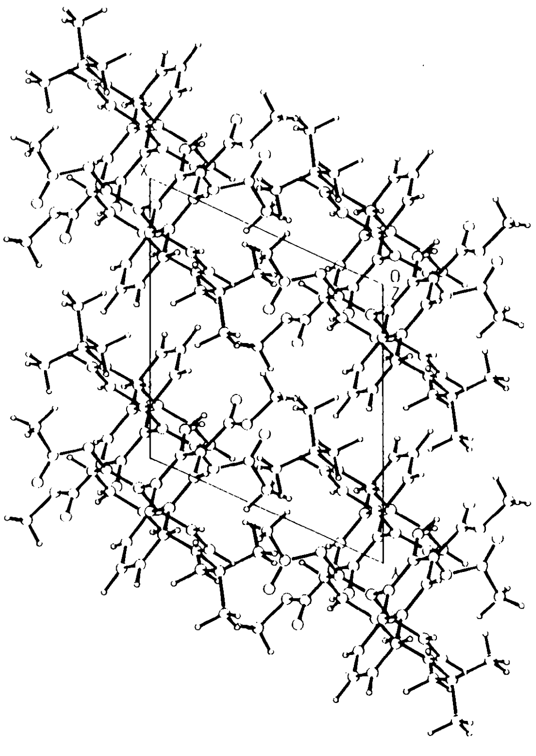

Fig. 2. Packing scheme of the title compound.

Acta Crystallographica Section C
ISSN 0108-2701 © 1994

Experimental

Crystal data

$C_{28}H_{26}O_5$
M_r = 442.51
Triclinic
$P\overline{1}$
a = 9.078 (3) Å
b = 10.848 (3) Å
c = 13.745 (4) Å
α = 110.73 (2)°
β = 95.59 (3)°
γ = 111.05 (2)°
V = 1141.8 (7) Å^3

Z = 2
D_x = 1.29 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 18 reflections
θ = 20.05-22.56°
μ = 0.082 mm^{-1}
T = 295 K
0.55 × 0.30 × 0.25 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4291 measured reflections
3934 independent reflections
3404 observed reflections [$I > 1.96\sigma(I)$]

$R_{\rm int}$ = 0.010
$\theta_{\rm max}$ = 25°
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -16 \rightarrow 16$
2 standard reflections
frequency: 120 min
intensity variation: −0.8%

Refinement

Refinement on F
R = 0.047
wR = 0.054
S = 1.352
3404 reflections
402 parameters
All H-atom parameters refined

$w = 1/(\sigma F_o^2 + 0.0009F_o^2)$
$(\Delta/\sigma)_{\rm max}$ = 0.007
$\Delta\rho_{\rm max}$ = 0.23 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.26 e Å^{-3}
Atomic scattering factors from *SHELX76* (Sheldrick, 1976)

SDP software (B. A. Frenz & Associates, Inc., 1985) was used for measurement, data reduction and cell refinement. Program used to solve structure: *SHELXS86* (Sheldrick, 1986). Program used to refine structure (by block-diagonal least squares in five blocks): *SHELX76* (Sheldrick, 1976). Program used to calculate molecular geometry: *PARST* (Nardelli, 1991).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.1475 (2)	0.1578 (1)	0.3078 (1)	0.0502 (6)
O2	0.3678 (2)	0.3471 (1)	0.2628 (1)	0.0656 (6)
O3	0.4151 (2)	0.2767 (1)	0.1009 (1)	0.0676 (7)
O1′	−0.2687 (1)	−0.0616 (1)	0.2229 (1)	0.0458 (5)
O2′	−0.4910 (2)	−0.2715 (2)	0.1527 (2)	0.1000 (9)
C1	0.0235 (2)	−0.0844 (2)	0.1787 (1)	0.0362 (7)
C2	0.1279 (2)	0.0585 (2)	0.2080 (1)	0.0367 (7)
C3	0.2141 (2)	0.1014 (2)	0.1357 (1)	0.0378 (7)
C4	0.1853 (2)	−0.0010 (2)	0.0338 (1)	0.0400 (7)
C5	0.0545 (3)	−0.2536 (2)	−0.1043 (2)	0.0539 (9)
C6	−0.0464 (3)	−0.3957 (3)	−0.1343 (2)	0.0674 (10)
C7	−0.1265 (3)	−0.4385 (2)	−0.0618 (2)	0.0681 (10)
C8	−0.1058 (3)	−0.3395 (2)	0.0390 (2)	0.0542 (8)
C9	−0.0021 (2)	−0.1904 (2)	0.0738 (1)	0.0389 (7)
C10	0.0793 (2)	−0.1475 (2)	−0.0001 (1)	0.0397 (7)
C11	0.3364 (2)	0.2526 (2)	0.1730 (2)	0.0469 (8)
C12	0.5389 (5)	0.4234 (3)	0.1326 (3)	0.0917 (15)
C1′	−0.0506 (2)	−0.1259 (2)	0.2612 (1)	0.0372 (7)
C2′	−0.1904 (2)	−0.1147 (2)	0.2820 (1)	0.0403 (7)
C3′	−0.2535 (2)	−0.1429 (2)	0.3646 (2)	0.0467 (8)
C4′	−0.1758 (2)	−0.1852 (2)	0.4275 (2)	0.0470 (8)
C5′	0.0527 (2)	−0.2428 (2)	0.4760 (1)	0.0420 (8)
C6′	0.1941 (2)	−0.2576 (2)	0.4613 (1)	0.0401 (7)
C7′	0.2512 (2)	−0.2325 (2)	0.3744 (1)	0.0441 (8)
C8′	0.1743 (2)	−0.1921 (2)	0.3100 (1)	0.0434 (8)
C9′	0.0299 (2)	−0.1737 (2)	0.3253 (1)	0.0361 (7)
C10′	−0.0321 (2)	−0.2024 (2)	0.4094 (1)	0.0379 (7)
C11′	−0.4243 (2)	−0.1490 (2)	0.1646 (2)	0.0521 (8)
C12′	−0.5004 (3)	−0.0736 (3)	0.1204 (2)	0.0630 (12)
C13′	0.2940 (2)	−0.2915 (2)	0.5359 (1)	0.0470 (8)
C14′	0.4621 (3)	−0.1617 (3)	0.5888 (2)	0.0621 (11)
C15′	0.3161 (4)	−0.4281 (3)	0.4703 (2)	0.0735 (14)
C16′	0.2136 (3)	−0.3164 (3)	0.6237 (2)	0.0599 (11)
HO1	0.229 (3)	0.241 (3)	0.312 (2)	0.081 (8)

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

O1—C2	1.358 (2)	C9—C10	1.424 (2)
O2—C11	1.217 (2)	C1′—C2′	1.365 (3)
O3—C11	1.322 (3)	C1′—C9′	1.432 (3)
O3—C12	1.454 (3)	C2′—C3′	1.399 (3)
O1′—C2′	1.418 (3)	C3′—C4′	1.360 (4)
O1′—C11′	1.348 (2)	C4′—C10′	1.416 (3)
O2′—C11′	1.187 (3)	C5′—C6′	1.375 (3)
C1—C2	1.375 (3)	C5′—C10′	1.418 (3)
C1—C1′	1.495 (2)	C6′—C7′	1.421 (2)
C1—C9	1.423 (2)	C6′—C13′	1.528 (3)
C2—C3	1.426 (2)	C7′—C8′	1.355 (3)
C3—C4	1.372 (2)	C8′—C9′	1.419 (3)
C3—C11	1.474 (2)	C9′—C10′	1.416 (2)
C4—C10	1.400 (3)	C11′—C12′	1.480 (5)
C5—C6	1.359 (3)	C13′—C14′	1.535 (3)
C5—C10	1.418 (3)	C13′—C15′	1.534 (4)
C6—C7	1.401 (4)	C13′—C16′	1.524 (3)
C7—C8	1.364 (3)	O2· · ·HO1	1.74 (3)
C8—C9	1.415 (3)	O1—HO1	0.92 (2)
C11—O3—C12	116.9 (2)	O1′—C2′—C1′	118.7 (1)
C2′—O1′—C11′	117.5 (2)	O1′—C2′—C3′	118.2 (2)
C2—C1—C9	119.6 (2)	C1′—C2′—C3′	122.9 (2)
C9—C1—C1′	121.6 (2)	C2′—C3′—C4′	119.9 (2)
C2—C1—C1′	118.7 (1)	C3′—C4′—C10′	120.5 (2)
O1—C2—C1	118.3 (1)	C6′—C5′—C10′	122.3 (2)
O1—C2—C3	120.7 (2)	C5′—C6′—C7′	116.7 (2)
C1—C2—C3	120.9 (1)	C5′—C6′—C13′	123.5 (1)
C2—C3—C4	119.0 (2)	C7′—C6′—C13′	119.7 (2)
C2—C3—C11	119.6 (2)	C6′—C7′—C8′	122.5 (2)
C4—C3—C11	121.4 (2)	C7′—C8′—C9′	121.5 (1)
C3—C4—C10	122.2 (1)	C1′—C9′—C10′	120.2 (2)
C6—C5—C10	120.6 (2)	C1′—C9′—C8′	122.7 (1)
C5—C6—C7	120.0 (3)	C8′—C9′—C10′	117.0 (2)
C6—C7—C8	121.1 (2)	C4′—C10′—C5′	121.2 (2)
C7—C8—C9	121.0 (2)	C4′—C10′—C9′	118.8 (2)
C1—C9—C8	122.5 (2)	C5′—C10′—C9′	119.9 (2)
C1—C9—C10	119.8 (2)	O1′—C11′—O2′	122.7 (2)
C8—C9—C10	117.7 (2)	O1′—C11′—C12′	112.3 (2)
C4—C10—C5	121.8 (2)	O2′—C11′—C12′	125.0 (2)
C4—C10—C9	118.5 (1)	C6′—C13′—C14′	108.0 (2)
C5—C10—C9	119.6 (2)	C6′—C13′—C15′	109.7 (1)
O2—C11—O3	122.1 (2)	C6′—C13′—C16′	112.4 (2)
O2—C11—C3	124.0 (2)	C14′—C13′—C15′	109.2 (2)
O3—C11—C3	113.9 (2)	C14′—C13′—C16′	108.9 (2)
C1—C1′—C2′	122.7 (2)	C15′—C13′—C16′	108.6 (2)
C1—C1′—C9′	119.7 (2)	O1—HO1· · ·O2	155 (2)
C2′—C1′—C9′	117.5 (2)		
C2—C1—C1′—C2′	85.8 (2)	C3—C2—O1—HO1	−6.1 (17)
C3′—C2′—O1′—C11′	−63.6 (2)	C4—C3—C11—O3	−1.5 (3)
C2′—O1′—C11′—O2′	−7.6 (3)	C5′—C6′—C13′—C16′	3.6 (3)

The binaphthol (3.3 g, 8.3 mmol) was suspended in 10 ml of acetic anhydride and the suspension refluxed for 50 min until the binaphthol had dissolved. The resulting bright yellow solution was cooled to approximately 293 K and a pale yellow precipitate formed. The crude product was isolated and recrystallized from acetic acid.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71381 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1053]

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Acta Cryst. (1994). C**50**, 139–141

Structure of an Oxepino[2,3-*b*]indolizine Derivative

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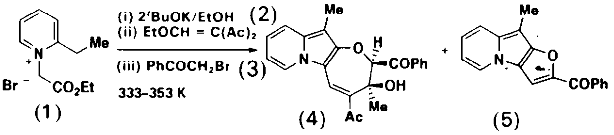
(*Received* 3 *March* 1993; *accepted* 30 *June* 1993)

Abstract

The pyrrole and pyridine rings in the indolizine skeleton of 4-acetyl-2-benzoyl-3-hydroxy-3,11-dimethyl-2,3-dihydrooxepino[2,3-*b*]indolizine, $C_{23}H_{21}NO_4$ (4), are planar, with mean deviations 0.007 (2) and 0.004 (3) Å, respectively, and are almost coplanar to one another with a dihedral angle of 2.2 (2)°. The seven-membered ring attached to positions 2 and 3 of the indolizine ring is slightly inclined to the indolizine ring by 6.1 (2)°. The phenyl ring in the benzoyl group at the 2 position of the oxepine ring is almost perpendicular to the indolizine ring with a dihedral angle of 91.8 (2)°. O4 of the acetyl group attached at the 4 position is hydrogen bonded to the 3-hydroxyl group in the same molecule [O4···O3 2.567 (3) Å].

Comment

An ethanolic solution (30 ml) of 2-ethyl-1-(ethoxycarbonylmethyl)pyridinium bromide (1) (3 mmol) was treated with potassium *tert*-butoxide (6 mmol) at 333–353 K in a water bath for 5 min. To the resulting solution, including 1-methyl-2(3*H*)-indolizinone (Kakehi, Ito, Watanabe, Kitagawa, Takeuchi & Hashimoto, 1980), ethoxymethyleneacetylacetone (2) (3 mmol) and phenacyl bromide (3) (3 mmol) were added and the mixture was then kept under the same conditions for 2 h. After removal of the solvent under reduced pressure, the residue was separated by column chromatography on alumina using ether and then chloroform to give (4) [27%, m.p. 472–474 K (from ethanol)] as orange prisms, together with 2-benzoyl-9-methylfuro[2,3-*b*]indolizine (5) (63%) (Kakehi, Ito, Ohizumi & Ito, 1983; Kakehi, Ito, Furuta & Todoroki, 1985). The acid-catalysed dehydration of (4) did not afford the corresponding fully conjugated oxepino[2,3-*b*]indolizine, rather its 3-methylene derivative.



The present study has been undertaken to confirm the chemical structure of the title compound (4) and to compare its structural features with those of some indolizines, especially those fused with oxygen-containing rings at the 2 and 3 positions. Comparative values of the selected bond lengths and angles for the indolizine moieties in the title compound (4) and other indolizine derivatives are summarized in Table 3. The bond distances and angles for the indolizine skeleton in (4) are similar to those in the non-fused ethyl 1-trifluoromethylindolizine-3-carboxylate (Pritchard, 1988), except the C5—C12 bond, which is more similar to the analogous bond in 3-acetyl-6-methyl-2*H*-pyrano[2,3-*b*]indolizin-2-one (Kakehi, Kitajima, Ito & Takusagawa, 1993) than that in 2-benzoyl-9-methylfuro[2,3-*b*]indolizine and 8-benzoyl-5,6-dihydro-4*H*-furo[2′,3′:4,5]pyrrolo[3,2,1-*ij*]quinoline (Kakehi, Kitajima, Ito & Takusagawa, 1994). These deviations are relatively small, but a slight extension of the N1—C10 bond of the