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Unique hydrogen bonding in the acetone-mediated helical structure of (*R*,*R*)-3,3′-bisBINOL

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Key indicators

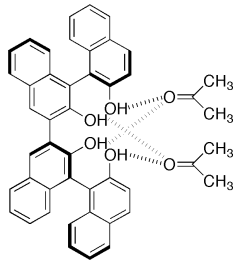
Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.100
Data-to-parameter ratio = 9.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The asymmetric unit of the title compound, $C_{40}H_{26}O_4\cdot 2(CH_3)_2CO$, consists of one molecule of (*R*,*R*)-3,3′-bisBINOL [(*R*,*R*)-1,1′:3′,3″:1″,1‴-quater-2-naphthol] and two acetone molecules. The central feature of the structure is the pair of unique sets of O—H···O···H—O hydrogen-bond arrangements between the two hydroxy groups of (*R*,*R*)-3,3′-bisBINOL and the O atom of acetone, which fixes the axial chirality of the 3,3′-bond as *S*, thus maintaining the helical structure of the bisBINOL in the *M* form.

Comment

Many natural compounds and pharmaceuticals possessing bioactivity are chiral, and their chiralities are in many cases directly related to their bioactivities, because they are recognized in different ways by chiral receptors. Thus the chemistry associated with chiral compounds, such as chiral recognition and asymmetric synthesis, is of particular importance. 1,1′-Bi-2-naphthol (BINOL) and its derivatives have been widely used in asymmetric synthesis, *e.g.* as effective chiral ligands for various metal complex catalysts. We recently succeeded in synthesizing a novel BINOL derivative, [(*R*,*R*)-1,1′:3′,3″:-1″,1‴-quater-2-naphthol], (I), abbreviated (*R*,*R*)-3,3′-bisBINOL, and preparing crystals from acetone that were suitable for X-ray analysis.



(I)

In 1984, Toda *et al.* reported the crystal structure of a 1:1 complex of (*R*)-BINOL and (*R*)-methyl *m*-tolyl sulfoxide, in which only one of the electron lone pairs of the sulfoxide O atom participates in the formation of a hydrogen bond. Also, the racemic complex of BINOL and acetone (Nassimbeni & Su, 2002) forms a 2:2 centrosymmetric O—H···O···H—O, hydrogen-bonded complex. On the other hand, each acetone O atom of complex (I) was found to be involved in a unique O—H···O···H—O hydrogen-bond arrangement, thus forming a 1:2 complex of (*R*,*R*)-3,3′-bisBINOL and acetone. More interestingly, the hydrogen bonds reside between the first and the third naphthol, and between the second and the fourth naphthol moieties, respectively; the axial chirality of the C3—C3′ (C13—C23 in Fig. 1) bond is therefore fixed as *S*,

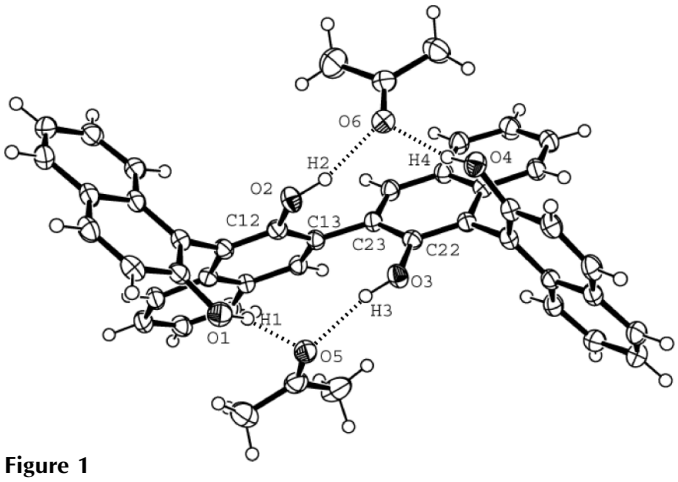


Figure 1
The structure of (I), with partial atomic numbering scheme, showing the hydrogen bonds as dashed lines. Displacement ellipsoids are drawn at the 50% probability level.

thus maintaining the helical structure of the bisBINOL in the *M* form.

The absolute configuration of (I) is based on the known configuration of (*R*)-BINOL, used as a starting material for the synthesis of the bisBINOL. This crystal structure is stabilized by the O1—H1···O5···H3—O3 and O2—H2···O6···H4—O4 hydrogen bonds (Fig. 1 and Table 1). The orientation between the two BINOL units is characterized by the C12—C13—C23—C22 torsion angle [62.1 (3)°].

Experimental

(*R*,*R*)-3,3′-BisBINOL was synthesized in two steps from (*R*)-2,2′-bis(methoxymethoxy)-3-iodo-1,1′-binaphthyl. To a solution of a catalytic amount of $NiBr_2(PPh_3)_2$ and zinc powder in tetrahydrofuran was added a solution of (*R*)-2,2′-bis(methoxymethoxy)-3-iodo-1,1′-binaphthyl in tetrahydrofuran, and the mixture was stirred overnight at 323 K. Acid hydrolysis of the reductive coupling product followed by chromatographic purification afforded (*R*,*R*)-3,3′-bisBINOL in 80% overall yield. Recrystallization of the product from acetone gave the corresponding acetone adduct, (I). Analysis calculated for $C_{40}H_{26}O_4{\cdot}2(CH_3)_2CO$: C 80.45, H 5.58%; found: C 80.38, H 5.53%. $[\alpha]_D^{22}$ = +249.15 (*c* = 1, acetone).

Crystal data

$C_{40}H_{26}O_4{\cdot}2C_3H_6O$
M_r = 686.76
Orthorhombic, $P2_12_12_1$
a = 13.403 (2) Å
b = 15.5692 (10) Å
c = 17.235 (2) Å
V = 3596.5 (7) Å^3
Z = 4
D_x = 1.268 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 38 232 reflections
θ = 3.0–27.5°
μ = 0.08 mm^{-1}
T = 93 (2) K
Block, colorless
0.60 × 0.55 × 0.50 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.952, T_{max} = 0.968
31 216 measured reflections
4540 independent reflections
4366 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 27.5°
h = −17 → 17
k = −20 → 20
l = −22 → 22

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.100
S = 1.09
4540 reflections
489 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 1.2636P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O5	0.95 (3)	1.94 (3)	2.854 (2)	160 (3)
O2—H2···O6	0.95 (4)	1.96 (4)	2.885 (2)	164 (3)
O3—H3···O5	0.94 (4)	1.98 (4)	2.889 (2)	163 (3)
O4—H4···O6	0.94 (4)	1.92 (4)	2.803 (2)	156 (3)

H atoms were positioned geometrically and refined as riding, with C—H = 0.95 Å (0.98 Å for methyl) and U_{iso}(H) = 1.2U_{eq}(C) [or 1.5U_{eq}(C) for methyl H atoms]. The H atoms bonded to O atoms were refined independently with isotropic displacement parameters. In the absence of significant anomalous dispersion effects, Friedel pairs were merged.

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2001); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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