

Conspicuous hydrogen bonds linking (*R,R*)-3',3''-bisBINOL, methyl 2-methylphenyl (*R*)-sulfoxide and chloroform in the 1:2:1 complex

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Key indicators

Single-crystal X-ray study
 $T = 93$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.033
 wR factor = 0.088
Data-to-parameter ratio = 17.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The asymmetric unit of the crystal structure of the title compound, $\text{C}_{40}\text{H}_{26}\text{O}_4 \cdot 2\text{C}_8\text{H}_{10}\text{OS} \cdot \text{CHCl}_3$, consists of one molecule of (*R,R*)-3',3''-bisBINOL [(*R,R*)-1,1':3',3''-1,1-*quater*-2-naphthol], two molecules of methyl 2-methylphenyl (*R*)-sulfoxide and one molecule of chloroform. The central feature of the structure is the two sets of $\text{O}-\text{H} \cdots \text{O} \cdots \text{H}-\text{O}$ hydrogen bonds, linking pairs of hydroxy groups of (*R,R*)-3',3''-bisBINOL *via* the sulfoxide O atoms and thus forming an 18-membered pseudo-macrocycle involving one bisBINOL and two sulfoxide molecules. The chloroform molecule is linked to one of the hydroxy O atoms of the bisBINOL *via* a $\text{C}-\text{H} \cdots \text{O}$ interaction.

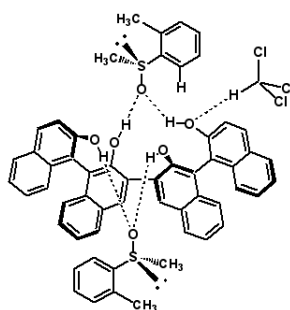
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Comment

Recently, we reported the crystal structure of an acetone adduct with axially chiral (*R,R*)-3',3''-bisBINOL [(*R,R*)-1,1':3',3''-1,1''-1'''-*quater*-2-naphthol] (Kawanami *et al.*, 2004). The observed conspicuous hydrogen bonding prompted us to prepare the corresponding chiral sulfoxide–bisBINOL adduct, to investigate the possibility of chiral recognition through such hydrogen bonding. In this paper, we report the results of an X-ray structural study of the chloroform solvate of the methyl 2-methylphenyl (*R*)-sulfoxide–bisBINOL adduct (I).



(I)

The asymmetric unit of the structure of the title compound consists of one molecule of (*R,R*)-3',3''-bisBINOL, two molecules of methyl 2-methylphenyl (*R*)-sulfoxide and one molecule of chloroform. The absolute configuration is based on the known configuration of (*R*)-BINOL, used as a starting material for the synthesis of (*R,R*)-3',3''-bisBINOL; the refinement of the Flack (1983) parameter confirmed this assignment.

Two sets of $\text{O}-\text{H} \cdots \text{O} \cdots \text{H}-\text{O}$ hydrogen-bonded patterns linking pairs of hydroxy groups of (*R,R*)-3',3''-bisBINOL *via* sulfoxide O atoms give rise to an 18-membered pseudo-macrocycle involving one bisBINOL and two sulfoxide molecules. Such an arrangement fixes the axial chirality with

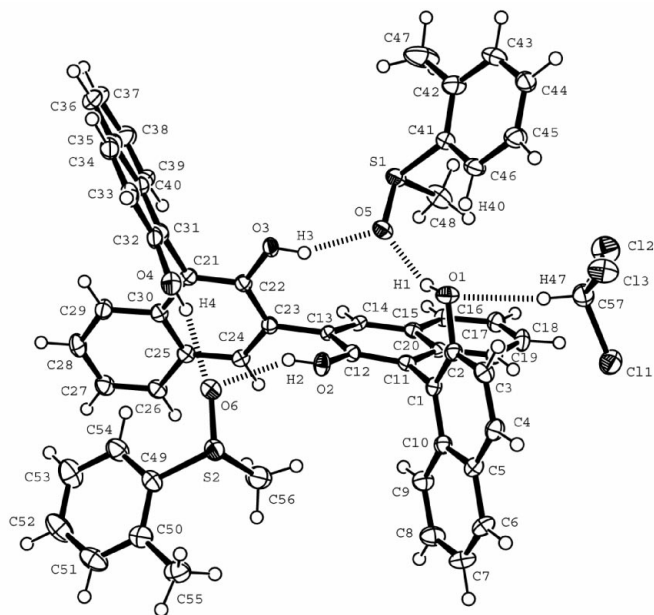


Figure 1

The structure of the title compound, with the atomic numbering scheme and hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level.

respect to the C3'–C3'' bond (C13–C23 in Fig. 1) as (*S*). The torsion angle about the C13–C23 bond, linking two BINOL units, shows that the latter units are roughly orthogonal [C12–C13–C23–C22 = 71.0 (2)°]. The torsion angles within each of the BINOL moieties are different [C2–C1–C11–C12 = –88.3 (2)° and C22–C21–C31–C32 = –71.1 (3)°], although both indicate an essentially orthogonal arrangement of the planes of the adjacent naphthalene systems.

Each of the two O–H···O···H–O systems (O1–H1···O5 and O3–H3···O5) is not exactly symmetrical. The O3···O5 distance [2.816 (2) Å] is longer than the O1···O5 distance [2.737 (2) Å]. On the other hand, the O2···O6 distance [2.767 (2) Å] is shorter than the O4···O6 distance [2.896 (2) Å]. The acidic chloroform CH group forms a hydrogen bond with one of the bisBINOL hydroxy O atoms [C57–H47···O1; C57···O1 = 3.319 (3) Å] acting as a 'terminal' branch attached to the hydrogen-bonded macrocycle. One more C–H···O interaction, involving the aromatic H atom *ortho* to the sulfoxide group (H40) and one of the bisBINOL hydroxy O atoms (O1), may also exist, judging from the C46···O1 distance [3.151 (3) Å] and the C46–H40···O1 angle [175 (3)°]. In contrast to the crystal structure of a 1:1 complex of (*R*)-BINOL and methyl 3-methylphenyl (*R*)-sulfoxide reported by Toda *et al.* (1984), where the two molecular components are alternately linked by hydrogen bonds to form infinite zigzag chains, all hydrogen bonds in the present structure are limited to one asymmetric unit and do not generate any crystal-wide motifs.

Experimental

A 1:2 mixture of (*R,R*)-3',3''-bisBINOL, derived from (*R*)-BINOL, and methyl 2-methylphenyl (*R*)-sulfoxide (90% *ee*), which was

synthesized according to Kagan's method (Pitchen & Kagan, 1984), was crystallized from chloroform. Analysis calculated for C₄₀H₂₆O₄·2C₈H₁₀OS·CHCl₃: C 68.57, H 4.74%; found: C 68.84, H, 4.74%.

Crystal data

C₄₀H₂₆O₄·2C₈H₁₀OS·CHCl₃
M_r = 998.42
 Orthorhombic, *P*2₁2₁2₁
a = 13.8789 (15) Å
b = 15.410 (2) Å
c = 22.705 (2) Å
V = 4856.0 (10) Å³
Z = 4
D_x = 1.366 Mg m^{–3}

Mo *K*α radiation
 Cell parameters from 41 152 reflections
 θ = 3.1–27.5°
 μ = 0.33 mm^{–1}
T = 93 (2) K
 Block, yellow
 0.8 × 0.8 × 0.6 mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995).
T_{min} = 0.779, *T_{max}* = 0.828
 40 838 measured reflections

11 046 independent reflections
 10 476 reflections with *I* > 2σ(*I*)
R_{int} = 0.040
 θ_{\max} = 27.5°
h = –15 → 18
k = –19 → 19
l = –29 → 28

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.033
wR(*F*²) = 0.088
S = 1.05
 11 046 reflections
 641 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 3.7498P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.007$
 $\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00146 (18)
 Absolute structure: Flack (1983), 4963 Friedel pairs
 Flack parameter = –0.01 (4)

Table 1

Selected torsion angles (°).

C12–C13–C23–C22	71.0 (2)	C12–C11–C1–C2	–88.3 (2)
C22–C21–C31–C32	–71.1 (3)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1–H1···O5	0.86 (4)	1.96 (3)	2.737 (2)	150 (3)
O2–H2···O6	0.84 (3)	2.03 (3)	2.767 (2)	147 (3)
O3–H3···O5	0.84 (3)	2.04 (3)	2.816 (2)	153 (2)
O4–H4···O6	0.87 (3)	2.08 (3)	2.896 (2)	155 (3)
C57–H47···O1	0.95 (3)	2.41 (3)	3.319 (3)	158 (2)
C46–H40···O1	0.93 (3)	2.23 (3)	3.151 (3)	175 (3)

H atoms bonded to O atoms and those bonded to C57 and C46 (involved in hydrogen bonding) were refined freely with isotropic displacement parameters. All other H atoms were positioned geometrically and included in the refinement in the riding-model approximation, with C–H = 0.95 Å (0.98 Å for methyl atoms) and *U*_{iso}(H) = 1.2*U*_{eq}(C) [1.5*U*_{eq}(C) for methyl atoms].

Data collection: *PROCESS-AUTO* (Rigaku Corporation, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK and Rigaku Corporation, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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