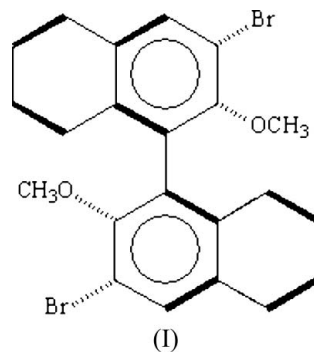


(R)-3,3'-Dibromo-2,2'-dimethoxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene: a Brønsted acid for catalyzing asymmetric Morita–Baylis–Hillman reactionsLong He^a and Seik Weng Ng^{b*}^aCollege of Chemistry and Chemical Engineering, China West Normal University, Nanchong 637002, People's Republic of China, and ^bDepartment of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

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Key indicatorsSingle-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.010$ Å
Disorder in main residue
 R factor = 0.067
 wR factor = 0.187
Data-to-parameter ratio = 15.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title compound, $\text{C}_{22}\text{H}_{24}\text{Br}_2\text{O}_2$, consists of two substituted tetralin units that are connected through a C–C single bond; the aromatic rings are twisted by $80.2(3)^\circ$.Received 30 October 2006
Accepted 6 November 2006**Comment**The title chiral bi-tetralin derivative, (I), is a Brønsted acid that catalyzes asymmetric Morita–Baylis–Hillman reactions (McDougal *et al.*, 2004; McDougal & Schaus, 2003). In the form of a molybdenum complex, the compound is also an efficient chiral catalyst for olefin metathesis (Schrock *et al.*, 2002). The compound was first synthesized a long time ago; then, it was used as a precursor for the synthesis of a chiral macrocycle having cavities that cannot be filled by conformational adaptations (Helgeson *et al.*, 1981). The crystal structure analysis in the present study confirms the axial chirality imposed by the two tetralinyl units as Br atoms are present (Fig. 1). The structure exhibits some disorder in both aliphatic portions; the aromatic rings, which are ordered, are aligned at $80.2(3)^\circ$.The crystal structures of several other chiral and non-chiral 2,2'-dihydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene derivatives have been reported. The unsubstituted homolog is known only in phosphorus (Cserepi-Szucs *et al.*, 1999; Guo *et al.*, 2002) and titanium (Eilerts *et al.*, 1994; Waltz *et al.*, 2004) compounds. Molybdenum complexes having 3-substituents (Aeilts *et al.*, 2001; Schrock *et al.*, 2002) and two other organic compounds (Goldberg, 1980; Knobler *et al.*, 1988; Reetz *et al.*, 1997) have also been reported.**Experimental**Crystals of the title compound were obtained by using a modification of a literature procedure (McDougal *et al.*, 2004; McDougal & Schaus, 2003). The synthesis used optically active (*R*)-1,1'-binaphthalene-2,2'-diol (BINOL) as the starting reactant.

(*R*)-BINOL (518 mg, 1.81 mmol) and Adams catalyst (platinum dioxide monohydrate) (52 mg, 0.21 mmol) were placed in acetic acid (14.5 ml). The mixture was stirred under hydrogen for 36 h. It was filtered through Celite and then diluted with chloroform (25 ml). The solution was washed with a saturated aqueous solution of sodium bicarbonate (50 ml); the organic phase was dried over sodium sulfate. The solvent was removed to afford (*R*)-2,2'-dihydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene. The hydrogenation was repeated several times to make larger quantities of the product.

The hydrogenated product (1.47 g, 5.00 mmol) in DMF (16 ml) was first treated with sodium hydride (60% *w/w* in oil, 840 mg, 35.0 mmol) in DMF (14 ml) at 273 K. Methyl iodide (2.84 g, 20.0 mmol) was added and the mixture stirred for another 0.5 h. The mixture was allowed to warm to room temperature over a period of 1.5 h. The mixture was again put back in the ice bath; water was added to destroy the sodium hydride that did not react. The white compound that separated from the aqueous solution was collected and dissolved in chloroform (30 ml). The solution was washed with water and then dried over sodium sulfate. Concentration of the organic layer afforded (*R*)-2,2'-dimethoxy-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthalene. The methylation was also repeated to make larger quantities of the product.

Bromine (3.00 g, 18.7 mmol) was added to the methylated compound (2.7 g, 8.3 mmol) dissolved in dichloromethane (85 ml) at 243 K. The solution was stirred for another 0.5 h; a saturated solution (70 ml) of sodium bicarbonate was added. The mixture was then allowed to warm to room temperature over a period of 1 h. The organic layer was washed with more sodium bicarbonate solution; it was dried over sodium sulfate. Concentration of the dichloromethane solution afforded colorless crystals of the title compound.

Crystal data

$C_{22}H_{24}Br_2O_2$	$Z = 4$
$M_r = 480.23$	$D_x = 1.631 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 9.778 (2) \text{ \AA}$	$\mu = 4.16 \text{ mm}^{-1}$
$b = 11.787 (2) \text{ \AA}$	$T = 295 (2) \text{ K}$
$c = 16.972 (3) \text{ \AA}$	Block, colorless
$V = 1956.1 (6) \text{ \AA}^3$	$0.26 \times 0.20 \times 0.12 \text{ mm}$

Data collection

Bruker SMART 1K area-detector diffractometer	10324 measured reflections
φ and ω scans	3842 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2505 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.422$, $T_{\max} = 0.635$	$R_{\text{int}} = 0.079$
	$\theta_{\text{max}} = 26.2^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1069P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.187$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 1.53 \text{ e \AA}^{-3}$
3842 reflections	$\Delta\rho_{\text{min}} = -0.79 \text{ e \AA}^{-3}$
247 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	1368 Friedel pairs
	Flack parameter: 0.00 (2)

The aliphatic portions of the tetralin units are disordered over two sites, which also affects the aromatic portions. The occupancies of the disordered atoms (C8/C8', C9/C9', C18/C18' and C19/C19') could not be refined, and were arbitrarily fixed as 0.5:0.5. For the aromatic portion, the C—C distances were restrained to 1.390 (5) Å. For the aliphatic portion, these were restrained to 1.500 (5) Å; additionally,

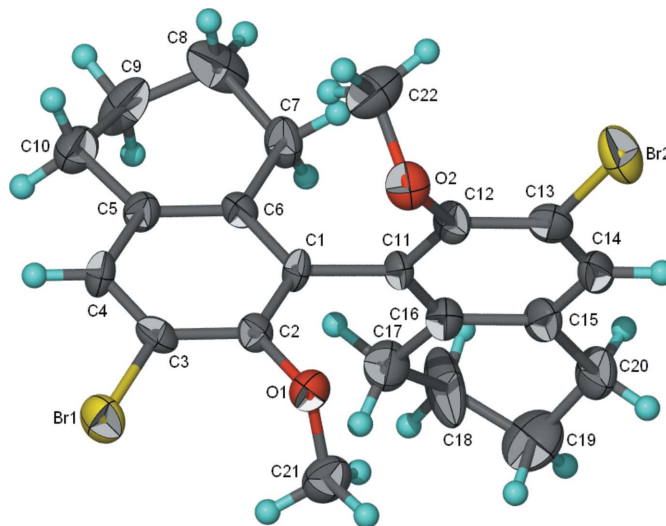


Figure 1

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level, and H atoms as spheres of arbitrary radii. Only one disorder component is shown.

the 1,3-related distances were restrained to 2.45 (1) Å. Somewhat tight restraints were used to avoid a spread of bond distances. The displacement parameters of the primed atoms were set equal to those of the unprimed atoms. C-bound H atoms were placed at calculated positions (C—H = 0.93–0.97 Å) and were included in the refinement in the riding-model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$. The final difference Fourier map had a large peak at about 1 Å from Br2.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: X-SEED (Barbour, 2001); software used to prepare material for publication: SHELXL97.

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