

(1*R,2*R**)-2-(Methylphenylamino)-1,2-dihydronaphthalen-1-ol-water (4/1)****Keith Fagnou, Mark Lautens and Alan J. Lough***

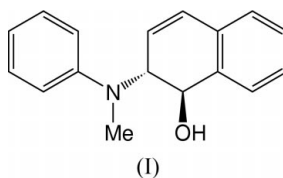
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Correspondence e-mail: alough@chem.utoronto.ca**Key indicators**Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.037
 wR factor = 0.090
Data-to-parameter ratio = 7.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The asymmetric unit of the title compound, $4\text{C}_{17}\text{H}_{17}\text{NO}\cdot\text{H}_2\text{O}$, contains four independent naphthalenol molecules and one molecule of water. All of the molecules in the asymmetric unit are connected into a contiguous row *via* $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. This unique hydrogen-bonded row is, in turn, linked to form extended $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonded chains, through unit-cell translations in the a direction. The hydrogen-bonding motif also contains an $\text{O}(\text{water})-\text{H}\cdots\pi(\text{arene})$ weak hydrogen bond, with an $\text{H}\cdots\text{Cg}$ distance of $2.64(4)$ Å (where Cg is the center of gravity of the phenyl ring).

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Recently, we reported a new rhodium-catalysed ring-opening reaction of 1,4-dihydro-1,4-epoxynaphthalene with a wide range of nucleophiles (Lautens *et al.*, 2000). The 1,2-regio-chemistry and the *trans* relative stereochemistry of the title compound, (I), were established by our X-ray diffraction analysis when *N*-methylaniline is used as the nucleophile.



In (I), the four independent molecules (Figs. 1–4) and the water molecule are linked into a contiguous row through $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds (see Table 2 and Fig. 5). This hydrogen-bonded unit is, in turn, linked into extended $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonded chains through unit-cell translations in the a direction. The binary-level graph set for this hydrogen-bonding motif is $C^5_5(10)$ (Bernstein *et al.*, 1995). Only one of the H-atom donors from the water molecule is involved in the above hydrogen-bonding motif. The other water H atom is involved in a weak $\text{O}(\text{water})-\text{H}\cdots\pi(\text{arene})$ bond [$\text{O1W}\cdots\text{Cg} = 3.384(3)$ Å, $\text{H2W}\cdots\text{Cg} = 2.64(4)$ Å and $\text{O1W}-\text{H2W}\cdots\text{Cg} = 148(3)^\circ$, where Cg is the center of gravity of the phenyl ring containing atoms $\text{C5A}/\text{C6A}/\text{C7A}/\text{C8A}/\text{C9A}/\text{C10A}$]. The values for the $\text{O}(\text{water})-\text{H}\cdots\pi(\text{arene})$ bond in (I) compare well with the mean values cited for other $\text{O}-\text{H}\cdots\pi(\text{arene})$ bonds (Desiraju & Steiner, 1999).

The bond lengths and angles in the four molecules of (I) (*A*, *B*, *C* and *D*) are the same within experimental error, although there appear to be some differences with respect to the degree of rotation about the $\text{C11}-\text{N1}$ and $\text{N1}-\text{C2}$ bonds (see Table 1 for relevant torsion angles). In the dihydronaphthalene group, an analysis (Cremer & Pople, 1975) of the puckering in the six-

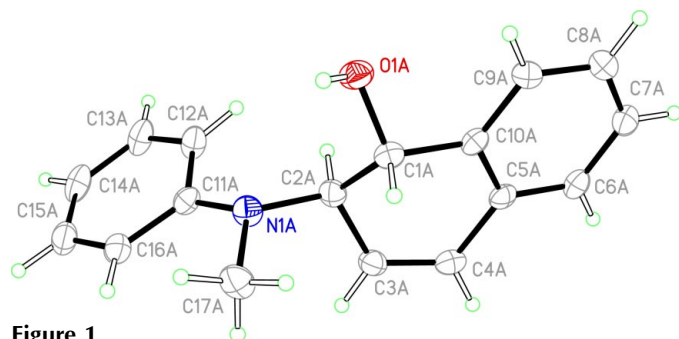


Figure 1
View of molecule *A* of (I), showing the crystallographic labelling scheme. Ellipsoids are at the 30% probability level.

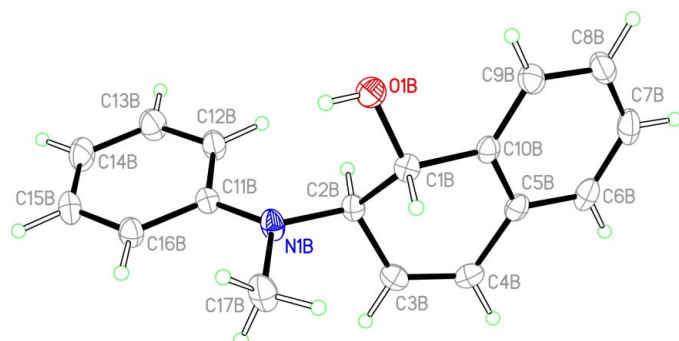


Figure 2
View of molecule *B* of (I), showing the crystallographic labelling scheme. Ellipsoids are at the 30% probability level.

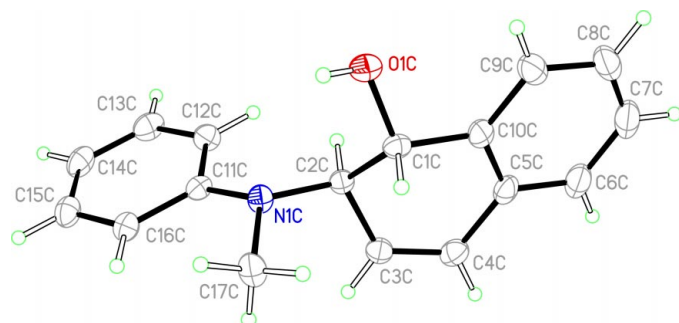


Figure 3
View of molecule *C* of (I), showing the crystallographic labelling scheme. Ellipsoids are at the 30% probability level.

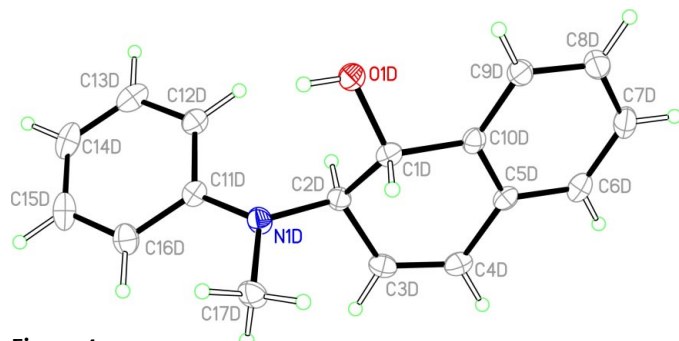


Figure 4
View of molecule *D* of (I), showing the crystallographic labelling scheme. Ellipsoids are at the 30% probability level.

membered ring (C1/C2/C3/C4/C5/C10) gives $Q_T = 0.440$ (3), 0.487 (3), 0.453 (3) and 0.411 (3) Å for molecules *A*, *B*, *C* and *D*, respectively. In all molecules, the conformation analysis of

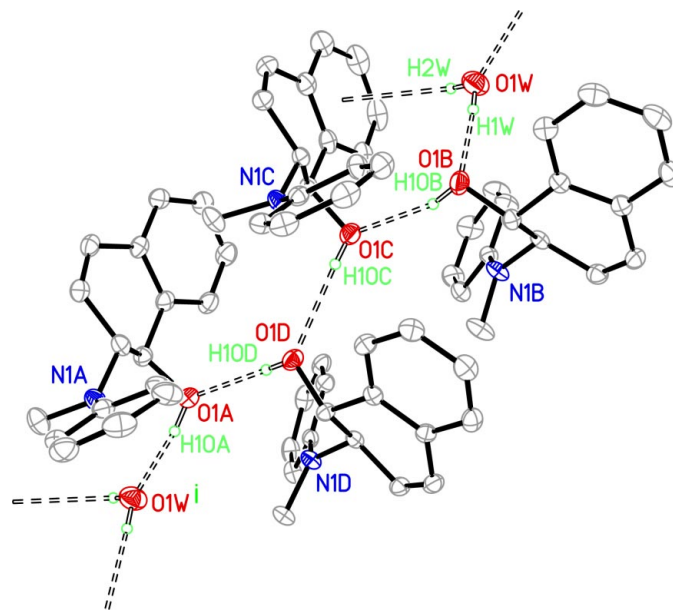


Figure 5
View of the asymmetric unit and the hydrogen bonding (shown with dashed lines), which connects the four title molecules and the water molecule. A symmetry-related molecule of water is included [symmetry code: (i) 1 + x , y , z] to indicate the extended hydrogen-bond motif.

that ring (Duax *et al.*, 1976) shows that the conformation is a half-chair, with a local pseudo-twofold axis running through the midpoints of the C1–C2 and C4–C5 bonds.

Experimental

The title compound was obtained as a colourless oil in 95% yield by treatment of 1,4-dihydro-1,4-epoxynaphthalene with *N*-methylaniline and catalytic $[\text{Rh}(\text{cyclooctadiene})\text{Cl}]_2$ and bis-(diphenylphosphino)-ferrocene in refluxing tetrahydrofuran. The oil was allowed to stand at room temperature for several weeks, during which time suitable crystals of (I) gradually formed.

Crystal data

$4\text{C}_{17}\text{H}_{17}\text{NO}\cdot\text{H}_2\text{O}$
 $M_r = 1023.28$
 Trigonal, $P3_1$
 $a = 12.3595$ (1) Å
 $c = 31.1411$ (4) Å
 $V = 4119.71$ (7) Å³
 $Z = 3$
 $D_x = 1.237$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 49468 reflections
 $\theta = 2.6\text{--}26.1^\circ$
 $\mu = 0.08$ mm⁻¹
 $T = 150$ (1) K
 Block, colourless
 0.25 × 0.24 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
 φ scans and ω scans with κ offsets
 49 468 measured reflections
 5415 independent reflections
 4878 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 26.0^\circ$
 $h = -15 \rightarrow 15$
 $k = -12 \rightarrow 15$
 $l = -38 \rightarrow 38$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.090$
 $S = 1.03$
 5415 reflections
 708 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.6948P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1Selected geometric parameters ($^{\circ}$).

C17A–N1A–C2A–C1A	–69.3 (3)	C17C–N1C–C2C–C1C	–69.7 (3)
C17A–N1A–C11A–C16A	3.6 (4)	C17C–N1C–C11C–C16C	14.4 (3)
C17B–N1B–C2B–C1B	–70.9 (3)	C17D–N1D–C2D–C1D	–78.9 (3)
C17B–N1B–C11B–C16B	5.3 (4)	C17D–N1D–C11D–C16D	–9.9 (4)

Table 2Hydrogen-bonding geometry (\AA , $^{\circ}$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1B–H1OB \cdots O1C	0.84	2.08	2.881 (3)	160
O1C–H1OC \cdots O1D	0.84	2.35	3.150 (3)	160
O1D–H1OD \cdots O1A	0.84	2.04	2.847 (3)	161
O1A–H1OA \cdots O1W ⁱ	0.84	1.89	2.716 (3)	169
O1W–H1W \cdots O1B	0.84	1.95	2.777 (3)	167

Symmetry code: (i) $1+x, y, z$.

All H atoms were included in calculated positions, with C–H distances of 0.95 (for sp^2), 1.00 (for sp^3), 0.98 (for methyl sp^3) and 0.84 \AA for O–H. They were then included in the refinement in riding-motion approximation, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ ($U_{\text{iso}} = 1.5U_{\text{eq}}$ for methyl) of the carrier atom. The H atoms of the water molecule were located in a difference Fourier map and refined with tight geometric restraints (O–H = 0.8400 ± 0.0001 \AA). Owing to the lack of anomalous scatterers, the absolute configuration was not determined from the X-ray diffraction data and Friedel pairs were merged. The enantiomer has been assigned by reference to analogous reactions

with an unchanging chiral ligand in the synthetic procedure.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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