

(*M*)- and (*P*)-8-[(1*S*,2*R*)-2-hydroxy-1-methyl-2-phenylethyl]-8-methyl-8,9-dihydro-7*H*-dinaphth[2,1-*c*:1',2'-*e*]azepinium bromide solvates

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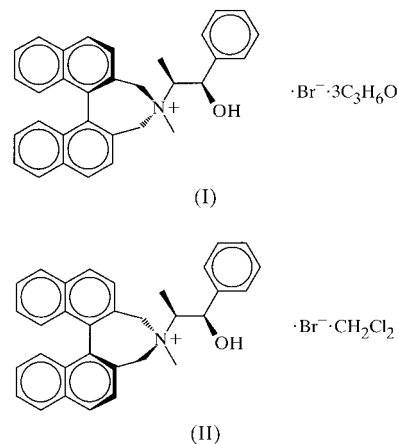
The title compounds are diastereoisomers with antipodean axial chirality. The *M* isomer crystallizes as a 1/3 acetone solvate, $C_{32}H_{30}NO^+ \cdot Br^- \cdot 3C_3H_6O$, while the *P* isomer crystallizes as a 1/1 dichloromethane solvate, $C_{32}H_{30}NO^+ \cdot Br^- \cdot CH_2Cl_2$. In each structure, $O-H \cdots Br$ hydrogen bonds link the cations and anions to give ion pairs. The seven-membered azepinium ring adopts the usual twisted-boat conformation and its ring strain causes a slight curvature of the plane of each naphthyl ring.

Comment

Axially chiral compounds containing a binaphthyl moiety have been used extensively as chiral auxiliaries for asymmetric synthesis, but the production of optically pure compounds of this type can be very tedious. Maigrot & Mazaleyra (1985) reported a relatively straightforward synthesis for obtaining a mixture of the *M*-1*S*,2*R* and *P*-1*S*,2*R* diastereoisomers of the title quarternary ammonium salts, (I) and (II), respectively, and found that these isomers could readily be separated by crystallization because of their markedly different solubilities in the usual organic solvents. Optically active azepinium compounds have been used in asymmetric phase transfer catalysis (Shi & Masaki, 1994). The corresponding dihydrobenzazepine compounds show pharmacological activity (Wenner, 1951; Hall *et al.*, 1986) and have been used as ligands in asymmetric catalysis (Widhalm *et al.*, 1998). We are currently using these conveniently resolved azepinium salts as precursors in the synthesis of new axially chiral diimine compounds, which can also act as potential ligands in asymmetric catalysis. As we are interested in the conformation of the seven-membered azepinium ring, as well as in the angle between the aromatic planes in the title compounds and in binaphthyl-diimines in general, we have determined the structures of (I) and (II).

In both (I) and (II), the bond lengths and angles are within normal ranges and an $O-H \cdots Br$ hydrogen bond exists

between the hydroxy group of the cation and the bromide ion, thus forming ion pairs. The asymmetric unit of compound (I) also contains three acetone molecules, which fit rather loosely into their cavities and show signs of disorder. The asymmetric unit of compound (II) includes a single ordered dichloromethane molecule.



The Cambridge Structural Database (CSD, October 1999 release; Allen & Kennard, 1993) contains the structures of ten dibenz- or dinaphthazepine derivatives, of which one is a dibenzazepinium salt (Alilou *et al.*, 1999) and three are neutral dinaphthazepines (Rychnovsky *et al.*, 1996; Widhalm *et al.*, 1998). Of these ten structures, three structures have sp^2 C atoms adjacent to the azepine N atom and one has no coordinates in the CSD. In the six remaining structures (Nyburg *et al.*, 1988; Rychnovsky *et al.*, 1996; Mrvoš-Sermek *et al.*, 1998; Widhalm *et al.*, 1998; Alilou *et al.*, 1999), the azepine or azepinium ring adopts a twisted-boat conformation in which one N—C bond and the opposing C—C bond that is fused to one of the naphthyl or phenyl rings forms the floor of the boat. The angle between the planes defined by this four-atom floor

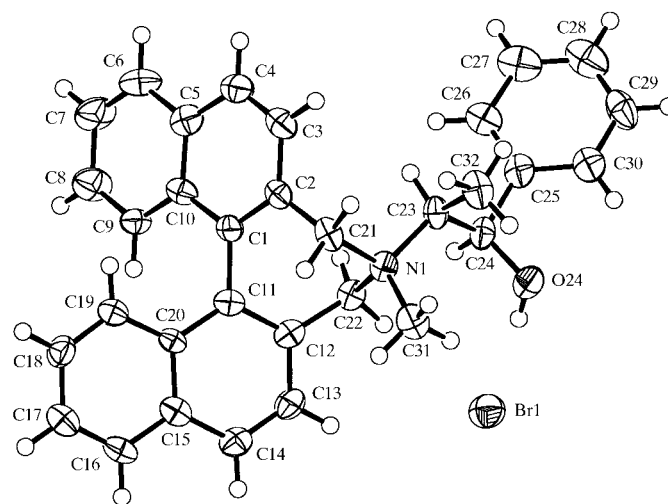


Figure 1
The molecular structure of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. The solvent molecules have been omitted for clarity.

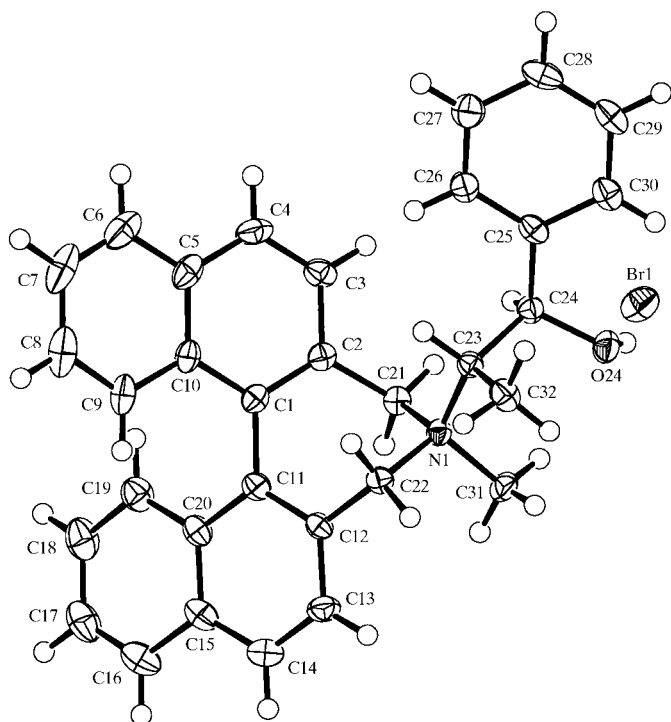


Figure 2
The molecular structure of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. The solvent molecule has been omitted for clarity.

and the three-atom bow plane of the boat is in the range 40.9–51.5°, while the angle between the floor and the four-atom stern plane of the boat is in the range 48.5–55.8°. The choice of the two alternatives for the definition of the boat, based on which N–C bond is used, makes little difference to these calculations. In (I) and (II), the corresponding plane angles are in a similar range, which shows that there is no significant difference between the conformations of azepine and azepinium rings. The angles between the mean plane through atoms N1, C11, C12 and C21 and the planes through N1, C12 and C22, and C1, C2, C11 and C21, are 49.7 (5) and 55.7 (3)°, respectively, for (I), and 44.3 (3) and 55.07 (13)°, respectively, for (II). Using the alternative definition of the boat atoms, the angles between the mean plane through atoms N1, C1, C2 and C22 and the planes through N1, C2 and C21, and C1, C11, C12 and C22, are 48.7 (5) and 55.5 (3)°, respectively, for (I), and 52.6 (2) and 54.24 (17)°, respectively, for (II).

The angle between the mean planes through each of the naphthyl rings is not significantly different for (I) and (II), being 59.66 (7) and 60.79 (7)°, respectively. The corresponding plane angle in the six database structures mentioned above is in the range 42.7–66.0°, with that in the dibenzazepinium salt (Alilou *et al.*, 1999) being 49.7°. However, in the structures of both (I) and (II), the naphthyl rings are not highly planar, with the r.m.s. deviation from the mean planes being 0.028 and 0.052 Å for the rings containing C1 and C11, respectively, in (I) and 0.064 and 0.045 Å, respectively, for the corresponding rings in (II). The deviation from planarity results primarily from a small bend about the C1···C4 and C11···C14 axes in

each compound, so that each naphthyl ring is composed of two much more planar subsections containing four and eight atoms. In (I), the maximum r.m.s. deviation in these sub-planes is only 0.018 Å and the angles between the planes that intersect along the C1···C4 and C11···C14 axes are 3.1 (4) and 7.9 (5)°, respectively. For compound (II), the corresponding angles are 10.09 (16) and 5.9 (3)°, respectively, with the maximum r.m.s. deviation in these sub-planes being 0.015 Å. The distortions of the naphthyl ring planes can be attributed to the effect of ring strain in the seven-membered azepinium ring which fuses with both naphthyl moieties in each compound. Despite these distortions, the bond lengths in the naphthyl rings show the usual pattern that is characteristic of naphthalene (Brock & Dunitz, 1982).

Curvature of the naphthyl ring plane is not unusual. Distortions of this nature appear to be quite common in 2,2'-substituted-1,1'-binaphthyl moieties when the 2 and 2' atoms are connected to each other *via* a seven-membered or smaller cyclic system, as in the case of compounds (I) and (II). The CSD contains 139 such entries with seven-membered rings composed of any element, and angles of up to 10° between the planes about the axes equivalent to C1···C4, as described above, are not uncommon. The mean of the sample is 4 (2)°. The CSD shows that larger interplanar angles of around 11 and 14° are found for six and five-membered connecting rings, respectively, which is indicative of the increasing effect of ring strain on the planarity of the naphthyl system. When there is no ring connecting the two naphthyl moieties, the distortions of the naphthyl rings are essentially negligible.

Experimental

The separated diastereoisomers, (I) and (II), were prepared according to the method of Maigrot & Mazaleyrat (1985). Crystals of (I) (m.p. 473–481 K) were obtained by slowly cooling a warm saturated solution of the compound in acetone to room temperature, while crystals of (II) (m.p. 531–537 K) were obtained by the slow diffusion of hexane into a saturated solution of the compound in dichloromethane.

Compound (I)

Crystal data

C₃₂H₃₀NO⁺·Br⁻·3C₃H₆O
M_r = 698.70
 Tetragonal, *P*4₁
a = 16.2515 (16) Å
c = 13.7964 (19) Å
V = 3643.8 (7) Å³
Z = 4
D_x = 1.274 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 22 reflections
 θ = 12.5–17.0°
 μ = 1.169 mm⁻¹
T = 173 (1) K
 Prism, colourless
 0.45 × 0.28 × 0.20 mm

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ -scan (North *et al.*, 1968)
 T_{\min} = 0.700, T_{\max} = 0.792
 8931 measured reflections
 4359 independent reflections plus 3673 Friedel-related reflections
 3936 reflections with $I > 2\sigma(I)$

R_{int} = 0.055
 θ_{max} = 27.50°
 h = -18 → 21
 k = -21 → 21
 l = -17 → 17
 3 standard reflections every 150 reflections
 intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.065$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.169$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.004$	$\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
8032 reflections	$\Delta\rho_{\min} = -0.41 \text{ e } \text{\AA}^{-3}$
432 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = -0.017 (13)

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O24—H24 \cdots Br1	0.84	2.35	3.182 (5)	172

Compound (II)

Crystal data

$C_{32}H_{30}NO^+ \cdot Br^- \cdot CH_2Cl_2$	$D_x = 1.407 \text{ Mg m}^{-3}$
$M_r = 609.40$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 22 reflections
$a = 8.234$ (3) \AA	$\theta = 13.5\text{--}17.5^\circ$
$b = 12.267$ (2) \AA	$\mu = 1.642 \text{ mm}^{-1}$
$c = 14.3806$ (19) \AA	$T = 173$ (1) K
$\beta = 98.015$ (15) $^\circ$	Plate, colourless
$V = 1438.3$ (5) \AA^3	$0.42 \times 0.30 \times 0.12 \text{ mm}$
$Z = 2$	

Data collection

Rigaku AFC-5R diffractometer	$R_{\text{int}} = 0.026$
$\omega/2\theta$ scans	$\theta_{\max} = 27.51^\circ$
Absorption correction: ψ -scan	$h = -10 \rightarrow 10$
(North <i>et al.</i> , 1968)	$k = -15 \rightarrow 15$
$T_{\min} = 0.596$, $T_{\max} = 0.821$	$l = -18 \rightarrow 18$
7400 measured reflections	3 standard reflections
3472 independent reflections plus	every 150 reflections
3142 Friedel-related reflections	intensity decay: none
5208 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.3206P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.096$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.017$	$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
6614 reflections	$\Delta\rho_{\min} = -0.32 \text{ e } \text{\AA}^{-3}$
345 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = -0.003 (8)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O24—H24 \cdots Br1	0.84	2.38	3.179 (2)	160

The data sets for compounds (I) and (II) included the Friedel opposites of all symmetry-unique reflections with $\theta < 25^\circ$ and $\theta < \theta_{\max}$, respectively. For both compounds, the methyl-H atoms were constrained to an ideal geometry with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, but were allowed to rotate freely about the C—C bonds. The orientation of the hydroxy-H atom was chosen initially by refining its position freely, whereupon it was found that the O—H vector was directed towards

the nearest Br atom. The position of the hydroxy-H atom was subsequently geometrically optimized while retaining this orientation and constrained to ride on its parent atom with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. There are three acetone molecules in the asymmetric unit of (I). They appear to fit rather loosely into their cavities and show evidence for being slightly disordered. As a result, the atomic displacement parameters for the solvent atoms are large and their bond lengths and angles are not ideal. In addition, the mean position for O3, which has the largest atomic displacement parameters, results in short intermolecular contacts of 2.80 and 2.94 \AA with C34 and C35, respectively, from another acetone molecule. Presumably, the true disordered positions for O3 are such that these interactions are minimized. Attempts to model the disorder were not fruitful, nor was an attempt to remove the solvent contribution by using the SQUEEZE procedure (van der Sluis & Spek, 1990) in PLATON (Spek, 2000). In the asymmetric unit of (II) there is one molecule of dichloromethane, which is not significantly disordered.

For both compounds, data collection: MSC/AFC Diffractometer Control Software (Molecular Structure Corporation, 1991); cell refinement: MSC/AFC Diffractometer Control Software; data reduction: TEXSAN (Molecular Structure Corporation, 1997); program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1391). Services for accessing these data are described at the back of the journal.

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