N2—C6—O3	109.8 (2)	C21—C20—C19	115.8 (3)
C6—O3—C7	121.1 (2)	C20—C21—C22	116.4 (3)
O3—C7—C9	109.0 (2)	C23—C22—C21	115.5 (3)
O3—C7—C10	111.4 (2)	C24—C23—C22	116.9 (4)
C9—C7—C10	112.4 (2)		
O1—C1—C2—N2	−37.3 (2)	C1—C2—N2—C6	−54.5 (2)
N1—C1—C2—N2	146.1 (2)	C2—N2—C6—O3	169.5 (2)
O1—C1—C2—C3	−164.4 (2)	N2—C6—O3—C7	165.0 (2)
N1—C1—C2—C3	19.0 (2)	C6—O3—C7—C8	−177.0 (2)
N2—C2—C3—C4	−166.7 (2)	C3—C4—O4—C11	−151.9 (2)
C1—C2—C3—C4	−40.6 (2)	C4—O4—C11—C12	−174.6 (2)
C2—C3—C4—O4	−63.4 (2)	O4—C11—C12—C13	102.9 (3)
C2—C3—C4—C5	56.1 (2)	C11—C12—C13—C14	178.2 (2)
O4—C4—C5—N1	69.4 (2)	C13—C14—C15—C16	−178.4 (3)
C3—C4—C5—N1	−48.7 (2)	C15—C16—C17—C18	180.0 (3)
O1—C1—N1—C5	169.4 (2)	C17—C18—C19—C20	179.5 (3)
C2—C1—N1—C5	−14.0 (3)	C19—C20—C21—C22	179.5 (3)
C4—C5—N1—C1	29.3 (3)	C21—C22—C23—C24	−178.6 (4)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O5	1.00 (2)	2.684 (3)	2.30 (2)	101.6 (13)
N1—H1N···O2^{i}	0.88 (2)	2.980 (3)	2.12 (2)	165 (2)
N2—H2N···O1^{ii}	0.86 (2)	2.910 (3)	2.06 (3)	175.4 (18)

Symmetry codes: (i) $2-x, -y, -z$; (ii) $2-x, 1-y, -z$.

Table 3. *Torsion angles (°) in the 2-piperidone rings of (I) and (II)*

	(I)	(II)
C4—C5—N1—C1	29.3 (3)	−26.8 (14)
C2—C1—N1—C5	−14.0 (3)	12.4 (14)
C1—C2—C3—C4	−40.6 (2)	48.1 (10)
N1—C1—C2—C3	19.0 (2)	−23.3 (12)
C2—C3—C4—C5	56.1 (2)	−62.9 (10)
C3—C4—C5—N1	−48.7 (2)	51.1 (11)

The structure was solved by direct methods. Most H atoms were located at difference Fourier maps except those bonded to the final atoms of the myristate chain (C16–C24). Those bonded to the C2, C3, C4, C5, N1 and N2 atoms were freely refined. H atoms of the *tert*-butyl group were all refined with the same C—H distance and U_{iso} value which converged to 0.99 (2) Å and 0.114 (4) Å^2, respectively. All H atoms belonging to the linear carbon chain were refined with $U_{iso} = 1.2U_{eq}$ of the parent atom and equal C—H distances [0.939 (16) Å], except for those bonded to C24 which were refined with $U_{iso} = 1.5U_{eq}$ of C24 and a C—H distance equal to that of the *tert*-butyl group.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *MSC/AFC Diffractometer Control Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994*a*) and *XPMA* (Zsolnai, 1994*b*). Software used to prepare material for publication: *PLATON*93 (Spek, 1993).

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(1*R*,2*R*)-(−)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine:† a Salen Ligand of Jacobsen's Catalyst

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Abstract

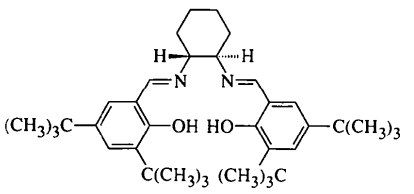
In the title compound, $C_{36}H_{54}N_2O_2$, two salicylideneimine moieties are situated nearly perpendicular to each other so that one of them has to be rotated for complexation. There are O—H···N intramolecular hydrogen bonds in both salicylideneimine moieties.

Comment

Cationic manganese(III) complexes of the salen ligand [*N*,*N*′-ethylenebis(salicylideneaminato)] are effective catalysts for the epoxidation of various olefins

† Alternative systematic name: 4,4′,6,6′-tetra-*tert*-butyl-2,2′-[1,2-cyclohexanediylbis(nitrilomethylidyne)]diphenol.

(Srinivasan, Michaud & Kochi, 1986). In particular, Mn complexes of the chiral salen ligands such as the title compound, (I), catalyze highly enantioselective epoxidation of unfunctionalized olefins (Chang, Lee & Jacobsen, 1993; Chang, Galvin & Jacobsen, 1994). The crystal structures of several complexes have been reported (Oki & Hodgson, 1990). We have determined the crystal structure of a chiral salen ligand, (I), in order to obtain information on its structural characteristics.



(I)

Both salicylideneimine moieties in (I) exist as the enol–imine form rather than the ketamine form. The enol O—C and imine C=N bond distances in the two moieties agree well with expected values, within experimental error, and their weighted averages are 1.363 (5) and 1.272 (5) Å, respectively. Molecular dimensions of the two moieties are also comparable with those in compounds containing the same moieties (Pahor *et al.*, 1976; Corden, Bishop, Errington & Wallbridge, 1996). The enol O—C bonds are longer by ~0.03–0.05 Å, while the imine C=N bonds are shorter by ~0.02 Å than those in the Mn^{III} complexes of similar salen ligands (Oki & Hodgson, 1990). The relative importance of the ketamine form in complexes was also noticed by Pahor *et al.* (1976) through comparison of a free ligand structure with its Co^{II} derivatives.

The two salicylideneimine moieties are planar, with maximum deviations of 0.07 (1) Å for N9 and 0.144 (5) Å for N16 from the phenyl rings *A* and *B*, respectively, in which C2 and C23 show maximum deviations of 0.004 (4) and 0.014 (6) Å from the *A* and *B* planes, respectively. The relative orientations of the two moieties, both of which are in an equatorial position, with respect to the central cyclohexyl ring are quite different, as manifested in the torsion angles of −134.4 (6)° for C8—N9—C10—C11 and −61.7 (7)° for C14—C15—N16—C17. The two planar groups are nearly perpendicular to each other, with a dihedral angle of 76.32 (7)°. The conformation of the title compound is obviously not appropriate for coordination to a metal centre and rotation of the moiety *A* about the N9—C10 bond is required.

There are intramolecular hydrogen bonds between the hydroxy and imine groups in both salicylideneimine moieties [O1···N9 2.604 (7), O1—H1 0.99 (8), H1···N9 1.68 (8) Å, O1—H1···N9 154 (7)°; O24···N16 2.602 (7), O24—H24 1.04 (9), H24···N16 1.65 (9) Å, O24—H24···N16 152 (7)°]. Molecular packing mainly consists of van der Waals interactions.

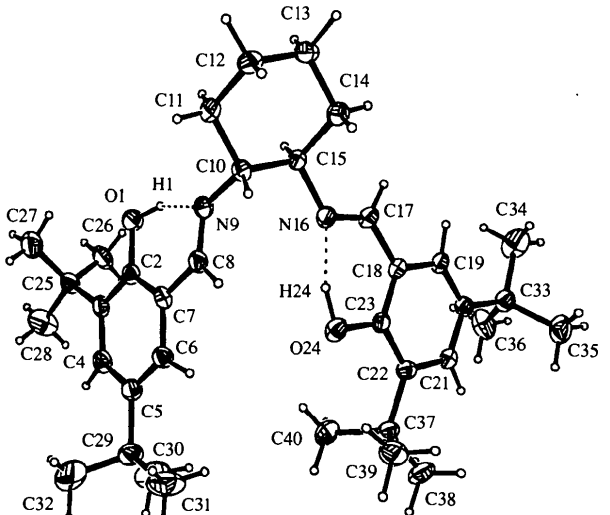


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The dotted lines denote hydrogen bonds.

Experimental

The title compound was purchased from Strem Chemicals, Inc. (Chemical Abstract Registry Number [135616-40-9]). Crystals were obtained from an ethanol–dichloromethane mixture by controlling solubility through the slow diffusion of ethanol from the aqueous to the organic phase (dichloromethane).

Crystal data

$C_{36}H_{54}N_2O_2$
M_r = 546.84
Orthorhombic
$P2_12_12_1$
a = 6.7832 (9) Å
b = 18.3250 (3) Å
c = 27.7510 (4) Å
V = 3449.5 (9) Å^3
Z = 4
D_x = 1.053 Mg m^{-3}
D_m = 1.07 Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 32 reflections
θ = 4.4–13.3°
μ = 0.064 mm^{-1}
T = 289 (2) K
Block
0.90 × 0.50 × 0.40 mm
Pale yellow

Data collection

Rigaku AFC-4 diffractometer
ω scans
Absorption correction: none
3469 measured reflections
3469 independent reflections
1941 reflections with $I > 2\sigma(I)$
θ_{max} = 25.0°
$h = -8 \rightarrow 0$
$k = -21 \rightarrow 0$
$l = -33 \rightarrow 0$
3 standard reflections
every 100 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.202$
$S = 1.065$
3462 reflections
432 parameters
H atoms were treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0884P)^2 + 1.5982P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.178$ e Å^{-3}
$\Delta\rho_{min} = -0.210$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0065 (13)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: assumed rather than determined

Table 1. *Selected geometric parameters (Å, °)*

O1—C2	1.365 (7)	C15—N16	1.484 (7)
C7—C8	1.462 (9)	N16—C17	1.272 (7)
C8—N9	1.271 (8)	C17—C18	1.451 (8)
N9—C10	1.476 (8)	C23—O24	1.361 (7)
O1—C2—C3	120.0 (5)	C17—N16—C15	118.6 (5)
O1—C2—C7	119.4 (6)	N16—C17—C18	123.4 (6)
C6—C7—C8	119.3 (6)	C23—C18—C17	121.9 (5)
C2—C7—C8	121.1 (6)	C19—C18—C17	118.3 (5)
N9—C8—C7	123.8 (6)	O24—C23—C18	119.4 (6)
C8—N9—C10	118.6 (5)	O24—C23—C22	120.1 (5)

Diffraction intensities from the crystals were generally weak and only 56% of the reflections were observed with $I > 2\sigma(I)$. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Methyl H atoms were generated geometrically and refined using the *AFIX* option of *SHELXL*93 (Sheldrick, 1993). The other H atoms were found from a difference Fourier map. The positions of the two hydroxy H atoms were refined with isotropic displacement parameters. The positions of all methyl H atoms and of the other H atoms were refined with displacement parameters 1.3 and 1.15 times the equivalent displacement parameters of the bonded atoms, respectively. It should be noted that the absolute structure was assumed from our purchase rather than determined from the Flack (1983) parameter which gives an unreasonable value in this case, the anomalous dispersion effects being too low.

Data collection: local program (Yoon, Kim & Shin, 1994). Cell refinement: local program (Yoon, Kim & Shin, 1994). Data reduction: local program (Yoon, Kim & Shin, 1994). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1304). Services for accessing these data are described at the back of the journal.

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1-Hydroxybaccatin I, $C_{32}H_{44}O_{14}$, and 2-Deacetoxydecinnamoyltaxinine J, $C_{28}H_{40}O_9$

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Abstract

The title compounds are diterpenoids isolated from the Himalayan yew (*Taxus wallichiana* Zucc.). The crystal structures allow us to rationalize some peculiar features of the NMR data of the taxane 4(20)-epoxides. Conformational differences between epoxide, olefin-type and oxetane-type compounds like paclitaxel are summarized.

Comment

Over the past decade, considerable attention has been given to taxoids (taxane diterpenoids), a small group of diterpenoids whose archetype is the anticancer drug paclitaxel (Taxol™; Appendino, 1995). There is much heated debate regarding the active conformation of this drug and numerous X-ray investigations have been performed on paclitaxel and other oxetane-type taxoids (Mastropaolo, Camerman, Luo, Brayer & Camerman, 1995, and references therein). The other classes of taxoids have received much less attention and as a result X-ray data are not yet available for taxanes of the 4(20)-epoxide type, the suspected biogenetic precursors of