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6,6′-Dimethoxy-2,2′-[(1*R*,2*R*)-cyclohexane-1,2-diylbis(nitrilomethylidyne)]diphenol: three C—H···O hydrogen bonds generate a three-dimensional framework

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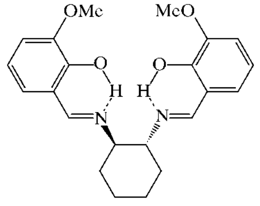
Molecules of the title compound, alternatively called (*R*,*R*)-*N*,*N*′-bis(3-methoxysalicylidene)-*trans*-cyclohexane-1,2-diamine, $C_{22}H_{26}N_2O_4$, contain two intramolecular O—H···N hydrogen bonds and adopt a conformation with approximate twofold rotational symmetry. The molecules are linked by three C—H···O hydrogen bonds [H···O = 2.45–2.55 Å, C···O = 3.329 (2)–3.398 (2) Å and C—H···O = 142–172°] into a continuous framework.

Comment

Chiral Schiff base complexes have been used as efficient catalysts for Michael reactions (Jha & Joshi, 2001), for epoxidation (Larrow & Jacobson, 1994) and for aziridination (Liang *et al.*, 2002) of alkenes. Furthermore, the N atoms of azomethine groups in metal complexes can act as hydrogen-bond acceptors, and it has been proposed that this interaction can account for some of the antibacterial and antifungal activities of ruthenium complexes (Ramesh & Sivagamasundari, 2003). The title compound, (I), was prepared as a forerunner to the synthesis and investigation of chiral ruthenium Schiff base complexes, and the present structural investigation was undertaken in order to assign unambiguously the structure and the hydrogen bonding.

The cyclohexane moiety adopts the usual chair conformation, with the two substituents in equatorial sites. There are two intramolecular O—H···N hydrogen bonds (Fig. 1), each forming an *S*(6) motif (Bernstein *et al.*, 1995), and these undoubtedly play a part in controlling the overall molecular conformation. This conformation is close to C_2 symmetry, but examination of the key torsion angles (Table 1) confirms the absence of exact twofold rotational symmetry. The bond distances show no unusual features, and the exocyclic C—C—O angles at C13 and C23 show the usual pattern (Seip & Seip, 1973; Ferguson *et al.*, 1996; Patterson *et al.*, 1998; Abonia *et al.*, 2003).



(I)

The absence of twofold rotational symmetry is also confirmed by the pattern and dimensions of the soft (Desiraju & Steiner, 1999) C—H···O hydrogen bonds (Table 2), where one phenyl ring, C11–C16, provides only one donor and one acceptor, while the other ring, C21–C26, provides two donors and two acceptors. These three hydrogen bonds serve to link the molecules into a continuous three-dimensional framework, whose description can be simplified by the use of the substructure approach (Gregson *et al.*, 2000).

Atom C14 in the molecule at (x, y, z) acts as a hydrogen-bond donor to phenolic atom O22 in the molecule at ($-\frac{1}{2}+x$, $-\frac{1}{2}-y$, $1-z$), while atom C14 at ($-\frac{1}{2}+x$, $-\frac{1}{2}-y$, $1-z$) in turn acts as a donor to atom O22 at ($-1+x$, y, z), so producing a *C*(14) chain running parallel to the [100] direction and generated by the 2_1 screw axis along (x, $-\frac{1}{4}$, $\frac{1}{2}$). At the same time, atom C24 at (x, y, z) acts as a donor to methoxy atom O23 at ($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$), so producing a *C*(4) chain

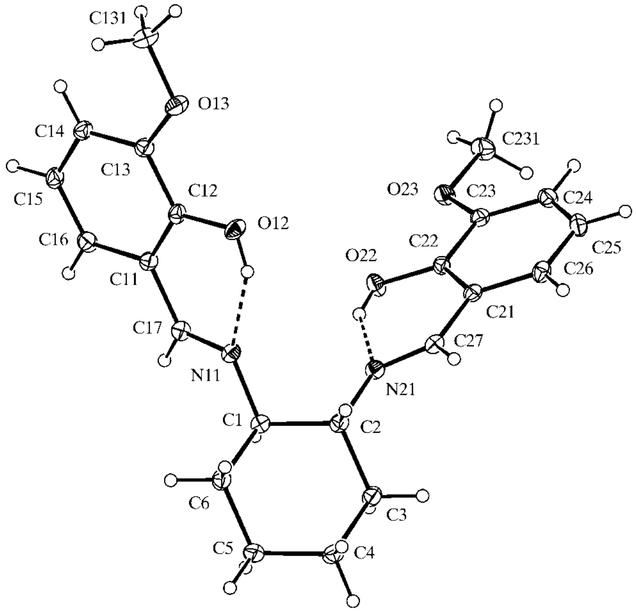


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids have been drawn at the 30% probability level.

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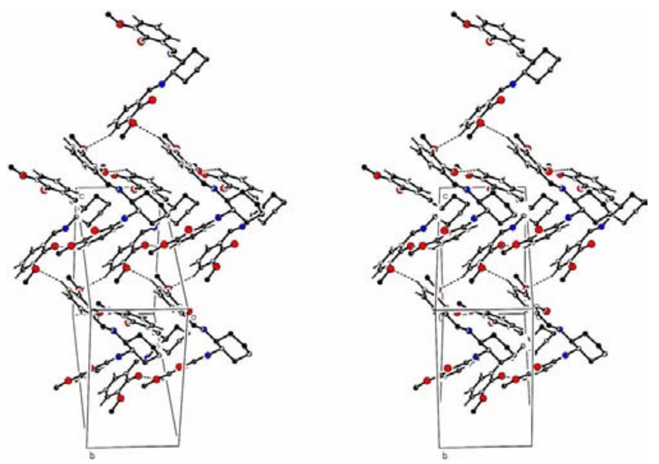

Figure 2
Stereoview of part of the crystal structure of (I), showing the formation of a (001) sheet of $R_4^4(38)$ rings.

around the 2_1 screw axis along $(x, \frac{1}{4}, \frac{1}{2})$. These two chain motifs combine to produce a (001) sheet in the form of a (4,4)-net (Batten & Robson, 1998) built from a single type of $R_4^4(38)$ ring (Fig. 2). Two sheets of this type pass through each unit cell, in the domains $0.23 < z < 0.77$ and $0.73 < z < 1.27$, and these sheets are linked into a single framework by the third of the C—H···O hydrogen bonds.

Atom C26 in the molecule at (x, y, z) acts as a hydrogen-bond donor to phenol atom O12 in the molecule at $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$, and propagation of this interaction produces a $C(12)$ chain running parallel to the [010] direction and generated by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ (Fig. 3). The molecules at (x, y, z) and $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ lie, respectively, in the $0.23 < z < 0.77$ and $0.73 < z < 1.27$ sheets. Similarly, atom C26 in the molecule at $(-\frac{1}{2} + x, -\frac{1}{2} - y, 1 - z)$, which also lies in the $0.23 < z < 0.77$ sheet, acts as a hydrogen-bond donor to atom O12 in the molecule at $(\frac{1}{2} - x, -1 - y, -\frac{1}{2} + z)$, which lies in the $-0.27 < z < 0.27$ sheet. Hence, this hydrogen bond links each (001) sheet to the two neighbouring sheets, so forming a single continuous framework.

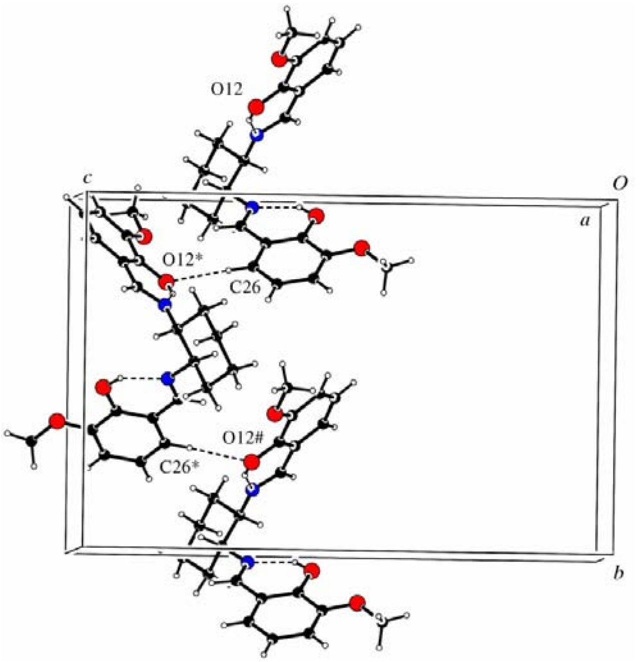

Figure 3
Part of the crystal structure of (I), showing the formation of the $C(12)$ chain that links the (001) sheets. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(x, 1 + y, z)$, respectively.

Experimental

The Schiff base was obtained by refluxing a mixture of 2-methoxysalicylaldehyde (20 mmol) and the L-(+)-tartaric acid salt of *trans*-(1*R*,2*R*)-1,2-diaminocyclohexane (10 mmol) in the presence of anhydrous potassium carbonate, with a methanol–water mixture as solvent. The crude product was obtained by removing the solvent at reduced pressure and was recrystallized from hexane (yield 85%; m.p. 401–403 K). Analysis found: C 69.5, H 6.4, N 7.2%; $C_{22}H_{26}N_2O_4$ requires: C 69.1, H 6.9, N 7.3%. IR (cm^{-1}): 3416 (OH), 1626 (C═N); NMR (CDCl$_3$): δ(H) 1.42–1.60 (*m*, 4H, CH$_2$), 1.86–1.96 (*m*, 4H, CH$_2$), 3.59 (*m*, 2H, CH), 3.93 (*s*, 6H, OCH$_3$), 6.3–7.2 (*m*, 6H, aromatic), 8.24 (*s*, 2H, CH═N), 13.81 (*s*, 2H, OH); $[\alpha]_D^{23}$ (CH$_3$OH): −46.9° dm^{-1} g^{-1} cm^3.

Crystal data

$C_{22}H_{26}N_2O_4$
$M_r = 382.45$
Orthorhombic, $P2_12_12_1$
$a = 7.5558$ (2) Å
$b = 13.4054$ (1) Å
$c = 20.0304$ (3) Å
$V = 2028.85$ (6) Å^3
$Z = 4$
$D_x = 1.252$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2642 reflections
$\theta = 3.0$–27.4°
$\mu = 0.09$ mm^{-1}
$T = 120$ (2) K
Plate, yellow
0.32 × 0.25 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.962$, $T_{\max} = 0.994$
27 432 measured reflections

2642 independent reflections
2484 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.071$
$\theta_{\max} = 27.4°$
$h = -9 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.084$
$S = 1.08$
2646 reflections
257 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.3696P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (°).

O13—C13—C12	115.06 (14)	O23—C23—C22	114.60 (15)
O13—C13—C14	125.21 (16)	O23—C23—C24	125.37 (15)
C2—C1—N11—C17	146.74 (15)	C1—C2—N21—C27	158.41 (15)
C1—N11—C17—C11	178.86 (14)	C2—N21—C27—C21	177.82 (15)
N11—C17—C11—C12	6.8 (2)	N21—C27—C21—C22	6.1 (2)
C12—C13—O13—C131	179.67 (15)	C22—C23—O23—C231	−176.88 (15)

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

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12···N11	0.84	1.84	2.580 (2)	147
O22—H22···N21	0.84	1.82	2.568 (2)	147
C14—H14···O22^{i}	0.95	2.50	3.329 (2)	146
C24—H24···O23^{ii}	0.95	2.55	3.356 (2)	142
C26—H26···O12^{iii}	0.95	2.45	3.398 (2)	172

Symmetry codes: (i) $x-\frac{1}{2}, -\frac{1}{2}-y, 1-z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (iii) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Crystals of (I) are orthorhombic and the space group $P2_12_12_1$ was uniquely assigned from the systematic absences. All H atoms were treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH_3), 0.99 (CH_2) or 1.00 Å (aliphatic CH), and O—H distances of 0.84 Å. In the absence of significant anomalous scattering, the Flack (1983) parameter was indeterminate (Flack & Bernardinelli, 2000); hence, the Friedel equivalents were merged before the final refinements, and the absolute structure was set by reference to the known *R*,*R* configuration of the *trans*-1,2-diaminocyclohexane used in the synthesis.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1640). Services for accessing these data are described at the back of the journal.

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