Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: none
5774 measured reflections
5372 independent reflections
4720 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.020$

$\theta_{\max} = 27.51°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 0$
$l = 0 \rightarrow 38$
3 standard reflections every 247 reflections intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.077$
$S = 1.046$
5372 reflections
293 parameters
H atoms treated by a mixture of constrained and independent refinement
$w = 1/[\sigma^2(F_o^2) + (0.0443P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 0.237$ e Å^{-3}
$\Delta\rho_{\min} = -0.283$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.06 (6), 2306 Friedel pairs

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

N—S1	1.6651 (18)	N′—S1′	1.6705 (18)
N—S2	1.6777 (18)	N′—S2′	1.6723 (17)
S1—O1	1.4306 (18)	S1′—O1′	1.4197 (19)
S1—O2	1.4319 (18)	S1′—O2′	1.4249 (18)
S1—C1	1.753 (2)	S1′—C1′	1.749 (3)
N—C10	1.493 (3)	N′—C10′	1.493 (3)
C10—C11	1.511 (3)	C10′—C11′	1.516 (3)
S1—N—S2	120.48 (11)	S1′—N′—S2′	120.48 (11)
C10—N—S1	120.79 (14)	C10′—N′—S1′	119.94 (14)
C10—N—S2	118.27 (14)	C10′—N′—S2′	118.86 (15)
O1—S1—N	108.38 (10)	O1′—S1′—N′	108.05 (10)
O2—S1—N	105.73 (10)	O2′—S1′—N′	105.83 (11)
O1—S1—C1	109.06 (12)	O1′—S1′—C1′	109.31 (13)
O2—S1—C1	107.97 (12)	O2′—S1′—C1′	107.98 (13)
N—S1—C1	105.62 (11)	N′—S1′—C1′	105.74 (12)
O1—S1—O2	119.25 (12)	O1′—S1′—O2′	119.13 (12)
N—C10—C11	113.72 (17)	N′—C10′—C11′	113.51 (18)
S2—N—S1—O1	39.91 (16)	S2′—N′—S1′—O1′	−39.00 (15)
S2—N—S1—O2	168.85 (13)	S2′—N′—S1′—O2′	−167.65 (12)
S2—N—S1—C1	−76.85 (15)	S2′—N′—S1′—C1′	77.95 (16)
S1—N—S2—O3	34.18 (16)	S1′—N′—S2′—O3′	−34.41 (14)
S1—N—S2—O4	162.81 (12)	S1′—N′—S2′—O4′	−162.51 (12)
S1—N—S2—C2	−81.89 (15)	S1′—N′—S2′—C2′	82.26 (15)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C10—H10*A*···O4$^{\text{i}}$	0.99	2.58	3.435 (3)	144
C10′—H10*D*···O4′$^{\text{ii}}$	0.99	2.36	3.172 (3)	139

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

Methyl H atoms were refined as rigid groups allowed to rotate but not tip; other H atoms riding.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). 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: FG1348). Services for accessing these data are described at the back of the journal.

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trans-(±)-*N*,*N*′-Bis(salicylidene)-1,2-cyclohexanediamine†

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Abstract

The title compound, $C_{20}H_{22}N_2O_2$, is C_2 symmetric with the two N atoms bonded to salicylidene groups which are *trans* with respect to the cyclohexane ring.

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† Alternative name: 2,2′-[1,2-cyclohexanediylbis(iminomethyl)]diphenol.

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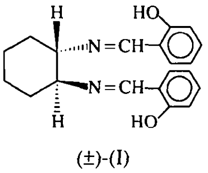
Comment

The typical Jacobson catalyst *N*,*N*'-bis(3,5-di-*tert*-butylsalicylidene)chloro-1,2-cyclohexadiamine–manganese (Jacobson, 1993) can be used to catalyse hydrogenation and epoxidation. Furthermore, it can also be occluded in an elastomeric type polymethylsiloxane membrane with the same catalytic activity (Vankelecom, Tas, Parton, Vyver & Jacobs, 1996). Recently, we tried synthesizing some organolanthanocenes with racemic and optically active Schiff bases. During this processing, the title compound, (I), was considered as a ligand.



(±)-(I)

In the title molecule, two N atoms are in *trans* positions. The bond distances of C1—N2 and C6—N1 are *ca* 0.2 Å longer than those of C14—N2 and C7—N1, demonstrating the double-bond character of the latter. The cyclohexane ring is non-planar with a maximum atomic deviation of 0.249 (1) Å, while the other two rings are planar. The two phenyl rings are inclined to the mean plane of the cyclohexane ring at 79.81 (10) and 78.12 (12)°, while they form an angle of 56.50 (13)° with each other.

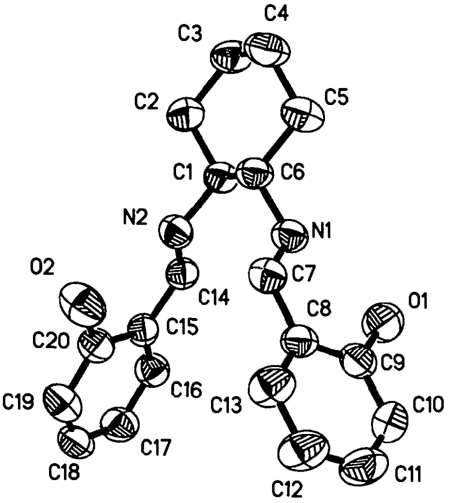


Fig. 1. The molecular structure of $C_{20}H_{20}O_2N_2$ showing the 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The synthesis of (I) was carried out by treatment of *trans*-(±)-1,2-cyclohexanediamine with 2.4 molar equivalents of salicylaldehyde in boiling toluene. Yellow prism crystals were obtained by crystallization from ethanol.

Crystal data

$C_{20}H_{22}N_2O_2$
$M_r = 322.40$
Monoclinic
Cc
$a = 16.001\,(1)$ Å
$b = 11.821\,(3)$ Å
$c = 9.641\,(1)$ Å
$\beta = 98.53\,(3)°$
$V = 1803.4\,(5)$ Å^3
$Z = 4$
$D_x = 1.187$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 4.47–12.59°$
$\mu = 0.077$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.42 × 0.36 × 0.14 mm
Yellow

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.271$, $T_{\max} = 0.295$
2489 measured reflections
2186 independent reflections

1423 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 26.98°$
$h = -1 \rightarrow 20$
$k = 0 \rightarrow 15$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 100 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.085$
$S = 0.869$
2186 reflections
282 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.094$ e Å^{-3}
$\Delta\rho_{\min} = -0.131$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C9	1.337 (4)	N1—C6	1.454 (4)
O2—C20	1.340 (4)	N2—C14	1.265 (4)
N1—C7	1.269 (4)	N2—C1	1.471 (4)
C7—N1—C6	118.4 (3)	N1—C6—C5	110.8 (3)
C14—N2—C1	119.0 (2)	N1—C6—C1	109.8 (2)
N2—C1—C2	110.0 (3)	N1—C7—C8	122.8 (3)
N2—C1—C6	108.8 (2)	N2—C14—C15	122.8 (3)

The structure was solved by direct methods. All H atoms were placed in ideal positions with common isotropic displacement parameters ($U_{\rm iso} = 0.08$ Å^2).

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *XL* in *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1061). Services for accessing these data are described at the back of the journal.

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Pseudosymmetry in 2,5-Dimethyl-1,4-benzenediol

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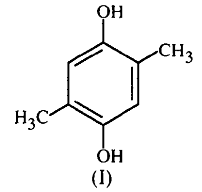
Abstract

The title compound, $C_8H_{10}O_2$, was prepared from diacetyl by a high temperature and pressure reaction. Pseudosymmetry in the structure results in diffraction symmetry enhancement for half the reflections and the possibility of twinning and stacking faults. The structure consists of two independent but pseudosymmetrically-related $P2_1/c$ substructures, each having centrosymmetric molecules on centres of inversion which are strongly hydrogen bonded to symmetry-related molecules to form layers perpendicular to $\mathbf{c}^*$. The structure may be described as an occupancy modulation, ordering a disordered parent structure in *Pnma* symmetry to form, upon change of axes, the $P2_1/c$ structure reported. The hydroxyl H atoms have two site options corresponding to alternative hydrogen-bonding patterns and the methyl H atoms in one substructure are rotationally disordered.

Comment

High temperature and pressure reactions utilizing indigenous materials led to a study of the reaction chemistry of diacetyl, resulting in the title compound, (I). A full quadrant of data was collected using a nearly orthorhombic *B*-centred cell [$a' = 13.211\,(4)$, $b' = 4.518\,(1)$, $c' = 23.655\,(8)$ Å and $\beta' = 89.50\,(3)°$]. A check on the Laue symmetry led to the observation that the structure is monoclinic ($R_{\rm int}$ for $2/m$ symmetry is 0.027), but reflections with l even define a pseudo-orthorhombic parent structure ($R_{\rm int}$ for pseudosymmetry operations is 0.075). Reflections with l odd have an $R_{\rm int}$ for pseudosymmetry operations of 0.91 and are clearly monoclinic. A primitive cell was then chosen and reflections re-indexed, so as to describe the $P2_1/c$ structure as reported.



(I)

The *B*-centred cell is described as $\mathbf{a}' = 2\mathbf{a} + \mathbf{c}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = \mathbf{c}$ relative to the reported cell for $P2_1/c$ and the pseudo-orthorhombic reflections describe an apparent scattering density with a primitive unit cell $\mathbf{a}'' = \mathbf{a}'/2$, $\mathbf{b}'' = \mathbf{b}'$, $\mathbf{c}'' = \mathbf{c}'/2$. Thus, $\mathbf{a}'' = \mathbf{a} + \mathbf{c}/2$, $\mathbf{b}'' = \mathbf{b}$ and $\mathbf{c}'' = \mathbf{c}/2$, and the structure can be thought of as an occupancy modulation [modulation vector $q = (\mathbf{a}''^* + \mathbf{c}''^*)/2$], ordering and distorting a disordered parent structure of $P2_1/n2_1/m2_1/a$ symmetry. Absence conditions $h'',k'',0$, h'' odd and $0,k'',l''$, $k'' + l''$ odd of *Pnma* become pseudo-absence conditions $h,k,0$, h odd and $h,k,-2h$, $h + k$ odd for the re-indexed reflections and the pseudo-equivalence of intensities relates reflections h,k,l and $-h-l,k,l$ with l even.

The symmetry operations associated with the $\mathbf{a}''$ and $\mathbf{c}''$ axes of *Pnma* must be destroyed in the ordered structure as otherwise the extra reflections will not be observed. However, pseudosymmetry operations can be used to describe the relationship between adjacent layers of the ordered structure. Using the cell $\mathbf{a},\mathbf{b},\mathbf{c}$ with $1-x$, $1-y$, $1-z$ chosen as the asymmetric unit for the second molecule, the relationship between layers may be described as: layer at $x = (2N+1)/2$ is obtained from layer at $x = N$ by operation $\frac{1}{2}+x$, y, $\frac{1}{2}+x-z$; layer at $x = N$ is obtained from layer at $x = (2N-1)/2$ by operation $\frac{1}{2}+x$, y, $x-z$, any N. Both these operations correspond to *a*-glide operations of *Pnma* for the cell $\mathbf{a}'',\mathbf{b}'',\mathbf{c}''$.

The odd and even layers belong to separate substructures of $P2_1/c$ symmetry. A pseudo-*a*-glide that transforms substructure 1 into substructure 2 also transforms substructure 2 into substructure 1 translated by $\mathbf{c}/2$. This corresponds to a re-orientation of the total structure. It also allows the possibility of alternative origins for individual layers. The consequence of such stacking faults has negligible effect on l even reflections but can be modelled as a scaling and twinning of l odd reflections