O5—S—O6	115.4 (3)	N—C9—C14	107.1 (4)
O5—S—O7	114.2 (3)	C10—C9—C14	114.8 (5)
O6—S—O7	110.1 (3)	C9—C10—C11	114.4 (5)
C4—O1—C5	104.4 (4)	C1—C11—C10	124.5 (6)
C3—O2—C18	117.3 (5)	C1—C11—C12	116.4 (6)
S—O4—C6	119.1 (3)	C10—C11—C12	118.9 (5)
C9—N—C16	113.8 (4)	C4—C12—C11	124.3 (6)
C9—N—C17	114.5 (5)	C4—C12—C13	109.0 (5)
C16—N—C17	111.5 (5)	C11—C12—C13	126.5 (5)
C2—C1—C11	121.0 (6)	C5—C13—C12	98.7 (4)
C1—C2—C3	122.1 (6)	C5—C13—C14	117.8 (4)
O2—C3—C2	119.8 (6)	C5—C13—C15	112.4 (4)
O2—C3—C4	122.6 (6)	C12—C13—C14	109.2 (4)
C2—C3—C4	116.9 (6)	C12—C13—C15	110.7 (4)
O1—C4—C3	128.2 (5)	C14—C13—C15	107.7 (4)
O1—C4—C12	112.3 (5)	C8—C14—C9	114.9 (5)
C3—C4—C12	119.2 (6)	C8—C14—C13	112.9 (4)
O1—C5—C6	108.4 (4)	C9—C14—C13	107.2 (4)
O1—C5—C13	104.6 (4)	C13—C15—C16	111.6 (5)
C6—C5—C13	115.4 (5)	N—C16—C15	111.7 (4)
O4—C6—C5	110.4 (4)	O2—C18—O3	123.1 (6)
O4—C6—C7	107.2 (5)	O2—C18—C19	110.5 (6)
C5—C6—C7	111.8 (4)	O3—C18—C19	126.3 (7)

The H atom attached to the N atom was located in a difference map at a late stage in the refinement. Thereafter the orientation of the N—H vector was fixed, but the N—H distance was allowed to vary [final value 0.96 (6) Å]. Difference maps also revealed disorder of the H atoms attached to C19. Equal occupancy factors and a rotation of 60° between two sets of positions were assumed.

Data collection: *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX/PC*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1191). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 125–127

N,*N*′-Bis(2-hydroxybenzylidene)-2,2-dimethyl-1,3-propanediamine

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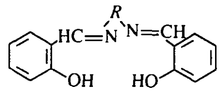
Abstract

In the title compound, $C_{19}H_{22}N_2O_2$, the average N···O separation of 2.580 (4) Å is indicative of intramolecular hydrogen bonding within each salicylideneimine unit. The two aromatic rings are inclined at an angle of 68.66 (11)° and this results in a conformation which is inappropriate for quadridentate ligand activity.

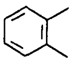
Comment

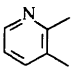
Although the crystal structures of many metal complexes with Schiff base ligands have been reported, very few of the free ligands have been similarly characterized (Calligaris & Randaccio, 1987). For quadridentate ligands of type (I), the solid-state structures have only been reported for (I*a*) (Pahor, Calligaris, Nardin & Randaccio, 1978), (I*b*) (Pahor *et al.*, 1976; Subrahmanyam, Seshasayee & Aravamudan, 1982), (I*c*) (Cimerman, Galesic & Bosner, 1992), (I*d*) (Senn & Nowacki, 1977), and (I*e*) (Elerman, Svoboda & Fuess, 1991). The structure of the title compound, (II), has now been determined so that subsequent changes upon coordination to a metal may be investigated.



(I)

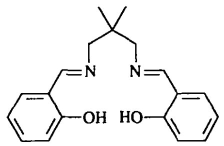
(I*a*) $R = CH_2—CH_2$

(I*b*) $R =$ 

(I*c*) $R =$ 

(I*d*) $R = CHPh—CHPh$

(I*e*) $R = CH_2—CH_2—CH_2$



(II)

The molecular structure of the title compound, as determined in this work, is represented in Fig. 1. Clearly, the enolimine tautomer is favoured over the ketamine form. This is evident from the observed O1—C1 and

O2—C19 bond distances of 1.356 (4) and 1.352 (4) Å, respectively, which are consistent with O—C single bonds; similarly the N1—C7 and N2—C13 distances of 1.284 (4) and 1.263 (3) Å are consistent with N═C double bonding. Furthermore, the N1—O1 and N2—O2 distances of 2.593 (4) and 2.566 (4) Å are clearly indicative of intramolecular hydrogen bonding; these distances are significantly shorter than the sum, 3.07 Å, of the van der Waals radii for nitrogen and oxygen (Bondi, 1964).

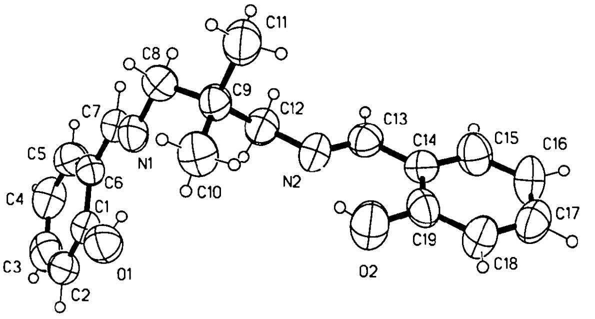


Fig. 1. View of the molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

The conformation of the free ligand in the solid state is of particular interest in relation to that required in a metal complex. The torsion angle N2—C12—C9—C8 is −174.0 (3)°, but the corresponding value for N1—C8—C9—C12 is only 62.9 (4)°; these angles are of the same order of magnitude (173 and 68°, respectively) as those calculated [using *PLUTO* (Motherwell & Clegg, 1978) on the Chemical Database Service at Daresbury (Allen *et al.*, 1991)] from the data reported for the closely related molecule (I*e*) (Elerman, Svoboda & Fuess, 1991). The overall effect is that the least-squares planes through the two aromatic rings are inclined at an angle of 68.66 (11)°. Clearly this conformation is inappropriate for direct coordination to a metal ion. This is further emphasized by the large O1···O2 donor atom separation of 6.621 (4) Å, which is to be compared with a value of 3.006 (3) Å when coordinated to Ti^{IV} (Corden, Errington, Moore & Wallbridge, 1995). In this conformation the molecule is chiral, but its absolute structure could not be determined on the basis of the calculated Flack parameter (Flack, 1983).

Experimental

The title compound was prepared (Hughes *et al.*, 1993) in high yield (80%) by the condensation of salicylaldehyde (60 mmol) with 2,2-dimethyl-1,3-propanediamine (30 mmol) in methanol (40 cm^3). Crystals suitable for the X-ray diffraction work were obtained by the slow evaporation of a saturated methanolic solution of the product.

Crystal data

$C_{19}H_{22}N_2O_2$
$M_r = 310.39$
Orthorhombic
$P2_12_12_1$
$a = 6.160 (4)$ Å
$b = 16.172 (6)$ Å
$c = 17.307 (7)$ Å
$V = 1724.1 (15)$ Å^3
$Z = 4$
$D_x = 1.196$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 250 reflections
$\theta = 2.35$–$25.00°$
$\mu = 0.078$ mm^{-1}
$T = 293 (2)$ K
Block
0.32 × 0.28 × 0.21 mm
Yellow

Data collection

Delft Instruments FAST TV area-detector diffractometer
Absorption correction: none
7793 measured reflections
2678 independent reflections

1163 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0859$
$\theta_{\rm max} = 25.00°$
$h = -4 \rightarrow 6$
$k = -18 \rightarrow 17$
$l = -19 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0378$
$wR(F^2) = 0.0773$
$S = 0.657$
2677 reflections
208 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0065P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.12$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.10$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.0705 (3)	0.7818 (2)	0.35934 (14)	0.0825 (8)
O2	0.1571 (3)	0.61579 (15)	0.01097 (14)	0.0880 (8)
N1	0.3990 (4)	0.6818 (2)	0.3533 (2)	0.0682 (9)
N2	0.4528 (4)	0.6483 (2)	0.1109 (2)	0.0635 (8)
C1	0.1916 (6)	0.8293 (2)	0.4074 (2)	0.0612 (10)
C2	0.1040 (6)	0.9022 (3)	0.4351 (2)	0.0737 (11)
C3	0.2217 (8)	0.9510 (2)	0.4850 (3)	0.0853 (13)
C4	0.4304 (7)	0.9281 (3)	0.5082 (2)	0.0837 (12)
C5	0.5178 (5)	0.8568 (3)	0.4781 (2)	0.0746 (11)
C6	0.4034 (5)	0.8051 (2)	0.4274 (2)	0.0579 (9)
C7	0.5032 (5)	0.7319 (2)	0.3972 (2)	0.0605 (10)
C8	0.5045 (5)	0.6068 (2)	0.3253 (2)	0.0716 (11)
C9	0.4435 (5)	0.5875 (2)	0.2417 (2)	0.0592 (9)
C10	0.1954 (5)	0.5776 (2)	0.2337 (2)	0.0821 (12)
C11	0.5562 (5)	0.5049 (2)	0.2178 (2)	0.0870 (12)
C12	0.5242 (5)	0.6578 (2)	0.1902 (2)	0.0661 (9)
C13	0.5838 (5)	0.6605 (2)	0.0560 (2)	0.0606 (9)
C14	0.5176 (6)	0.6548 (2)	−0.0247 (2)	0.0556 (9)
C15	0.6588 (5)	0.6713 (2)	−0.0842 (2)	0.0759 (11)
C16	0.5982 (6)	0.6677 (3)	−0.1602 (2)	0.0828 (12)
C17	0.3881 (7)	0.6455 (2)	−0.1772 (2)	0.0783 (12)
C18	0.2429 (6)	0.6274 (2)	−0.1200 (2)	0.0711 (11)
C19	0.3071 (6)	0.6328 (2)	−0.0438 (2)	0.0635 (10)

Table 2. *Selected geometric parameters (Å, °)*

O1—C1	1.356 (4)	N2—C12	1.450 (3)
O2—C19	1.352 (4)	C6—C7	1.432 (4)
N1—C7	1.284 (4)	C8—C9	1.527 (4)

N1—C8	1.458 (4)	C9—C12	1.528 (4)
N2—C13	1.263 (3)	C13—C14	1.458 (4)
C7—N1—C8	119.9 (3)	C8—C9—C12	108.6 (3)
C13—N2—C12	120.2 (3)	C10—C9—C11	109.2 (3)
O1—C1—C6	120.2 (4)	N2—C12—C9	112.0 (3)
N1—C7—C6	121.6 (3)	N2—C13—C14	122.2 (3)
N1—C8—C9	112.1 (3)	O2—C19—C14	121.7 (3)
O1—C1—C6—C7	1.8 (5)	C8—C9—C12—N2	−174.0 (3)
C1—C6—C7—N1	−3.9 (5)	N2—C13—C14—C19	−2.2 (5)
N1—C8—C9—C12	62.9 (4)	C13—C14—C19—O2	−0.1 (5)

H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl and hydroxyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached. Refinement was on all reflections except for one flagged by the user for potential systematic errors.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1992). Cell refinement: *MADNES*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1029). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Cyano-6-(3-methoxyphenyl)-4-methylthio-2-pyranone†

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Abstract

In the crystal structure of the title compound, $C_{14}H_{11}NO_3S$, the asymmetric unit consists of two molecules having different conformations. The main difference involves the orientation of the methoxy groups, but the angles between the two six-membered rings also differ slightly. This is the first reported structure of a δ-lactone with methylthio and cyano substituents.

Comment

Substituted δ-lactones are useful intermediates in the synthesis of various biologically active naturally occurring pyrones such as anibine, phenylcoumalin, paracotoin and xangonin (Tominaga, Ushirogochi & Matsuda, 1987; Tominaga, Ushirogochi, Matsuda & Kobayashi, 1977). They are also well known for their medicinal (Tominaga, Ushirogochi, Matsuda & Kobayashi, 1984) and synthetic applications (Ram, Hussaini, Singh & Shoeb, 1993). We have synthesized several lactones and subjected them to antibacterial and antifungal activity screening. In this context, the title phenyl-substituted δ-lactone, (I), has been prepared and its X-ray structure is reported here. It would appear to be the first reported structure of a δ-lactone with methylthio and cyano substituents.

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† Alternative nomenclature: 6-(3-methoxyphenyl)-4-methylthio-2-oxo-3-pyrancarbonitrile.