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Instrumental Achievements

Crystal Structure of *N*,*N*′-Bis(4-hydroxysalicylidene)-1,2-phenylenediimine, Methanol Solvate

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Although numerous transition-metal complexes of Schiff bases have been structurally characterized, relatively few free Schiff bases have been similarly characterized.[1] *N*-Substituted salicylaldimines show photochromism and thermochromism in the solid state. These effects are produced by intramolecular proton transfer associated with a change in the π-electron configuration.[2] As part of a general study of tetradentate Schiff bases, we determined the structure of the *N*,*N*′-bis(4-hydroxysalicylidene)-1,2-phenylenediimine, methanol solvate.

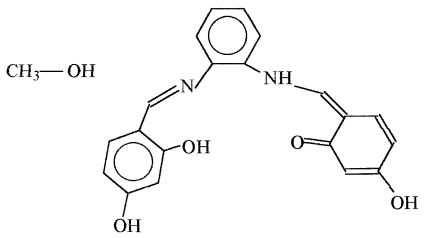

Fig. 1 Chemical structure.

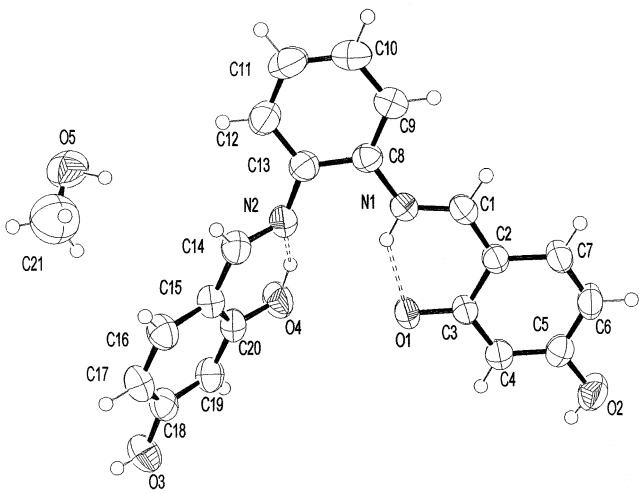

Fig. 2 Molecular structure of the title compound, while also showing the atom labeling scheme and 50% probability level displacement ellipsoids.

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The investigated compound was synthesized according to a well-established method.[3]

Several non-planar tetradentate Schiff bases similar to the title compound have been reported.[3] The title molecule is not planar. The salicylaldimine parts (**A** (C1, C2, C3, C4, C5, C6, C7, O1, O2) and **B** (C14, C15, C16, C17, C18, C19, C20, O3, O4)) are rotated relative to the phenylenediamine bridge, and the angles between the phenylenediamine bridge and the salicylaldimine parts **A** and **B** are 2.51(7)° and 50.21(4)°, respectively. Two types of intramolecular hydrogen bond (either N–H···O or N···H–O) can exist in Schiff bases.[1] In the title compound, there are both types of intramolecular hydrogen bonds. One of the intramolecular hydrogen bonds occurs between N1 and O1 as an N–H···O type (2.609(2)Å). This is evident from the observed O1–C3 bond distance of 1.305(2)Å, which is consistent with O=C double bonding; similarly, the C1–N1 distance of 1.312(2)Å is consistent with the N–C single bonds. The other intramolecular hydrogen bond is between N2 and O4 as a N···H–O type (2.651(2)Å). This is evident from the observed O4–C20 bond distance of 1.348(2)Å, which is consistent with O–C single bonds; similarly, the C14–N2 distance of 1.290(2)Å is consistent with N=C double bonding. The H1N of N1, H4O of O4 and H5O of O5 atoms were located from a difference Fourier map at the end of the refinement process as a small positive electron density and were refined isotropically. Apart from the intramolecular hydrogen bonds, there are two

Table 1 Crystal and experimental data

Formula: $C_{21}H_{20}N_2O_5$	
Formula weight = 380.39	
Crystal system: triclinic	
Space group: $P\bar{1}$	$Z = 2$
a = 11.122(2)Å	α = 97.32(1)°
b = 11.619(2)	β = 100.97(3)°
c = 8.529(1)	γ = 116.26(1)°
V = 945.1(2)Å^3	
D_x = 1.337 g/cm^3	
R =0.047	Rw = 0.145
$(\Delta/\sigma)_{max}$ = 0.001	
$(\Delta\rho)_{max}$ = 0.522 eÅ^{-3}	
$(\Delta\rho)_{min}$ = –0.369 eÅ^3	
No. of reflections used = 3882	
Measurements: Enraf-Nonius CAD-4 diffractometer	
Program system: CAD-4 EXPRESS Software	
Structure determination: SHELXS86	
Refinement: full-matrix least-squares (MolEN)	

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	B_{eq}/Å^2
N1	0.4325(1)	0.4172(2)	0.2565(2)	3.48(5)
N2	0.1521(2)	0.2716(2)	0.1513(2)	4.00(5)
O1	0.4126(1)	0.2298(1)	0.4062(2)	4.61(5)
O2	0.8326(1)	0.2551(2)	0.7012(2)	5.40(6)
O3	-0.2485(2)	-0.2175(1)	0.4013(2)	5.45(5)
O4	0.1087(1)	0.0318(2)	0.1752(2)	5.13(6)
C1	0.5672(2)	0.4695(2)	0.3191(2)	3.58(5)
C2	0.6291(2)	0.4130(2)	0.4184(2)	3.40(5)
C3	0.5481(2)	0.2906(2)	0.4587(2)	3.58(6)
C4	0.6185(2)	0.2376(2)	0.5537(2)	4.11(7)
C5	0.7615(2)	0.3024(2)	0.6089(2)	4.01(6)
C6	0.8409(2)	0.4228(2)	0.5700(3)	4.53(7)
C7	0.7766(2)	0.4761(2)	0.4777(2)	4.20(6)
C8	0.3613(2)	0.4661(2)	0.1537(2)	3.47(6)
C9	0.4287(2)	0.5836(2)	0.1073(2)	4.19(7)
C10	0.3529(3)	0.6260(2)	0.0074(3)	4.84(8)
C11	0.2104(3)	0.5516(3)	-0.0475(3)	5.3(1)
C12	0.1419(2)	0.4348(2)	-0.0023(3)	4.78(8)
C13	0.2157(2)	0.3903(2)	0.1007(2)	3.81(6)
C14	0.396(2)	0.2426(2)	0.1967(2)	4.18(7)
C15	-0.0362(2)	0.1228(2)	0.2461(2)	3.90(5)
C16	-0.1484(2)	0.1052(2)	0.3108(3)	4.64(8)
C17	-0.2214(2)	-0.0066(2)	0.3622(3)	4.72(8)
C18	-0.1829(2)	-0.1057(2)	0.3494(2)	4.20(6)
C19	-0.0741(2)	-0.0931(2)	0.2836(2)	4.26(6)
C20	0.0001(2)	0.0204(2)	0.2337(2)	3.91(6)
O5	-0.3485(2)	0.0232(2)	-0.2623(3)	6.92(8)
C21	-0.3831(5)	0.0107(4)	-0.1212(6)	14.81(8)
H1N	0.384(2)	0.344(2)	0.285(3)	
H4O	0.150(3)	0.122(3)	0.148(3)	

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\boldsymbol{a}_i \cdot \boldsymbol{a}_j)$.

intermolecular hydrogen bonds between O2 and O5^{i} (2.656(2)Å) and O3 and O1^{ii} (2.638(2)Å) [symmetry code: (i) $x + 1$, y, $z + 1$, (ii) $-x$, $-y$, $-z + 1$]. Table 1 shows the crystal and experimental data, while the final atomic parameters are given in Table 2.

Table 3 Selected bond distances (Å) and angles (°)

N(1) - C(1)	1.312(2)
N(1) - C(8)	1.412(2)
N(2) - C(14)	1.290(2)
N(2) - C(13)	1.410(2)
O(1) - C(3)	1.305(2)
O(2) - C(5)	1.348(2)
O(3) - C(18)	1.356(2)
O(4) - C(20)	1.348(2)
O(5) - C(21)	1.334(5)
C(1) - N(1) - C(8)	127.6(2)
C(14) - N(2) - C(13)	129.0(2)
N(1) - C(1) - C(2)	123.7(2)
O(1) - C(3) - C(4)	121.3(2)
O(1) - C(3) - C(2)	121.5(2)
O(2) - C(5) - C(4)	123.8(2)
O(2) - C(5) - C(6)	116.5(2)
C(9) - C(8) - N(1)	123.9(2)
C(13) - C(8) - N(1)	116.7(2)
C(12) - C(13) - N(2)	123.4(2)
C(8) - C(13) - N(2)	118.2(2)
N(2) - C(14) - C(15)	124.8(2)
O(3) - C(18) - C(19)	127.0(2)
O(3) - C(18) - C(17)	122.3(2)
O(4) - C(20) - C(19)	129.5(2)
O(4) - C(20) - C(15)	120.9(2)

The bond distances and angles are given in Table 3.

References

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