Amide H atoms refined; others riding with fixed U_{iso}

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—O1	1.225 (2)	C12—C13	1.377 (3)
C1—N2	1.337 (3)	C13—C14	1.360 (4)
C1—N1	1.390 (3)	C14—C15	1.353 (4)
N1—C2	1.357 (3)	C15—C16	1.391 (3)
C2—O2	1.203 (2)	C21—C26	1.377 (3)
C2—C3	1.551 (3)	C21—C22	1.386 (3)
C3—N2	1.461 (3)	C22—C23	1.379 (3)
C3—C21	1.528 (3)	C23—N3	1.339 (3)
C3—C11	1.533 (3)	N3—C25	1.324 (3)
C11—C16	1.374 (3)	C25—C26	1.389 (3)
C11—C12	1.385 (3)		
O1—C1—N2	128.0 (2)	C16—C11—C3	120.9 (2)
O1—C1—N1	124.1 (2)	C12—C11—C3	120.4 (2)
N2—C1—N1	107.8 (2)	C13—C12—C11	120.5 (2)
C2—N1—C1	112.4 (2)	C14—C13—C12	120.6 (3)
O2—C2—N1	127.6 (2)	C15—C14—C13	119.5 (2)
O2—C2—C3	126.2 (2)	C14—C15—C16	121.1 (3)
N1—C2—C3	106.1 (2)	C11—C16—C15	119.7 (2)
N2—C3—C21	112.7 (2)	C26—C21—C22	117.8 (2)
N2—C3—C11	110.75 (15)	C26—C21—C3	121.7 (2)
C21—C3—C11	112.9 (2)	C22—C21—C3	120.5 (2)
N2—C3—C2	100.7 (2)	C23—C22—C21	119.2 (2)
C21—C3—C2	108.08 (15)	N3—C23—C22	123.8 (2)
C11—C3—C2	111.0 (2)	C25—N3—C23	115.9 (2)
C1—N2—C3	112.7 (2)	N3—C25—C26	124.8 (2)
C16—C11—C12	118.5 (2)	C21—C26—C25	118.4 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^i	0.82 (3)	2.02 (3)	2.832 (2)	169 (3)
N2—H2···N3^{ii}	0.88 (3)	2.08 (3)	2.950 (3)	173 (2)

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

Data collection: *P3/PC* (Siemens, 1989). Cell refinement: *P3/PC*. Data reduction: *SHELXTL* (Siemens, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

References

Barnela, S. B., Worley, S. D. & Williams, D. E. (1987). *J. Pharm. Sci.* **76**, 245–247.

Burkett, H. D., Faison, J. H., Kohl, H. H., Wheatley, W. B., Worley, S. D. & Bodor, N. (1981). *Water Resour. Bull.* **7**, 874–879.

Camerman, A. & Camerman, N. (1971). *Acta Cryst.* B**27**, 2205–2211.

Chattopadhyay, T. K., Palmer, R. A. & Lisgarten, J. N. (1993). *J. Crystallogr. Spec. Res.* **23**, 149–152.

Codding, P. W. (1984). *Acta Cryst.* C**40**, 2071–2074.

Eknoian, M. W., Webb, T. R., Worley, S. D., Fleury, J. R. & Maddox, S. D. (1998). *Acta Cryst.* C**54**, 1529–1532.

Kohl, H. H., Wheatley, W. B., Worley, S. D. & Bodor, N. (1980). *J. Pharm. Sci.* **69**, 1292–1295.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1989). *P3/PC Diffractometer Program.* Version 3.13. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *SHELXTL.* Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Uno, T. & Shimizu, N. (1980). *Acta Cryst.* B**36**, 2794–2796.

Worley, S. D. & Burkett, H. D. (1984). *Water Resour. Bull.* **20**, 365–368.

Worley, S. D. & Williams, D. E. (1988). *Crit. Rev. Environ. Control.* **18**, 133–175.

Worley, S. D., Williams, D. E. & Barnela, S. B. (1987). *Water Res.* **21**, 983–988.

6-[*N*-(2-Hydroxyphenyl)aminomethylene]-cyclohexa-2,4-dien-1-one

Alok K. Mukherjee,[a] Rajib Lal De,[b] Indrajit Banerjee,[b] Chitra Samanta[a] and Nirmalya P. Nayak[a]

[a]*Department of Physics, Jadavpur University, Calcutta 700 032, India, and* [b]*Department of Chemistry, Jadavpur University, Calcutta 700 032, India. E-mail: akm@juphys.ernet.in*

Abstract

The structure determination of the title compound, $C_{13}H_{11}NO_2$, establishes the tautomeric keto form of the salicylaldimine. The asymmetric unit consists of two crystallographically independent molecules which are essentially planar and are approximately orthogonal to each other. Strong intramolecular N—H···O and intermolecular O—H···O interactions influence the conformation of the molecules and the crystal packing. Intermolecular hydrogen bonds link the molecules in infinite chains.

Comment

Salicylaldimines have been used extensively as ligands in coordination chemistry because of their diverse chelating ability (Long, 1995; Garnovski *et al.*, 1993). The intramolecular hydrogen bond between O and N atoms in these systems plays a vital role in the formation of Schiff base compounds in the solid state by proton transfer from the hydroxyl-O atom to the imine-N atom (Hadjoudis *et al.*, 1987; Elerman *et al.*, 1997). The charge transfer through overlapping intermolecular π-orbitals, with the associated change in the π-electron configuration in these compounds, also provides a basis for the development of molecular switches (Xu *et al.*, 1994). This X-ray crystallographic study was undertaken in order to establish the solid-state molecular structure of (I) and to build up a hierarchy for N-substituted salicylaldimines.

A structure with this salicylaldimine in enol form was reported by Elerman *et al.* (1995), based on poor quality data (18% intensity decay and affected by disorder). In the present crystals, the salicylaldimine takes the tautomeric keto form. The asymmetric unit of the title compound, (I), consists of two crystallographically independent, but nearly identical, molecules (*A* and *B*) which are approximately orthogonal to each other; the dihedral angle between the essentially planar molecules *A* (r.m.s. deviation 0.117 Å) and *B* (r.m.s. deviation 0.120 Å) is 84.55 (3)°. The torsion angles C6—N1—C7—C8 179.4 (1) and C19—N2—C20—C21 179.9 (1)° also illustrate that the molecules are almost planar. The C—O(hydroxyl) [1.348 (2) and 1.354 (2) Å in *A* and *B*, respectively] and N—C(phenyl) [1.412 (2) and 1.412 (2) Å in *A* and *B*, respectively] bond lengths are consistent with typical values in related compounds (Elerman *et al.*, 1995; Elmali & Elerman, 1997). The imine-N atoms (N1 and N2) are sp^2 hybridized with bond angles summing to 360.0°. Each displays trigonal planar bonding geometry and the coplanarity of the resulting pseudo-rings (N1, C7, C8, C13, O2, H1N in *A* and N2, C20, C21, C26, O4, H2N in *B*) strongly suggests a resonance interaction in the pseudo-rings. This is reflected in the deviations of the C7—C8 [1.416 (2)], C20—C21 [1.410 (2)], C13—O2 [1.294 (2)] and C26—O4 [1.297 (2) Å] bond lengths from standard C=C and C=O distances. A similar observation has been reported for 1-[*N*-(4-methyl-2-pyridyl)aminomethylene]-2(1*H*)-naphthalenone (Elerman *et al.*, 1998).
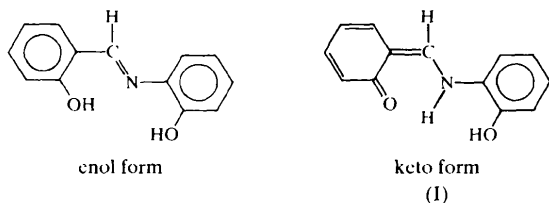
Strong intra- and intermolecular N—H···O and O—H···O interactions influence the conformations of molecules *A* and *B*, and the crystal packing. The atoms H1N and H2N were located from a difference Fourier map at the end of the refinement process as small positive electron densities. In molecule *A*, the N1—H1N and H1N···O2 distances are 0.851 and 1.852 Å, respectively, while the corresponding values in *B* for N2—H2N and H2N···O4 are 0.867 and 1.850 Å, respectively. The planarity of the molecules in (I) makes it possible for the proton to transfer through the hydrogen bond with a small energy requirement (Bregman *et al.*, 1964). Unlike the observations of Elerman *et al.* (1995) for the enol form of (I), *N*-(2-hydroxyphenyl)-salicylaldimine, the present structure analysis does not show any disorder of the molecule or intramolecular O···O hydrogen bonding. The crystal packing is stabi-

lized by intra- and intermolecular hydrogen bonds *via* oxo- and hydroxyl-O atoms. The molecules are linked by O—H···O hydrogen bonds into infinite chains with the sequence $A \cdots B \cdots A \cdots B$
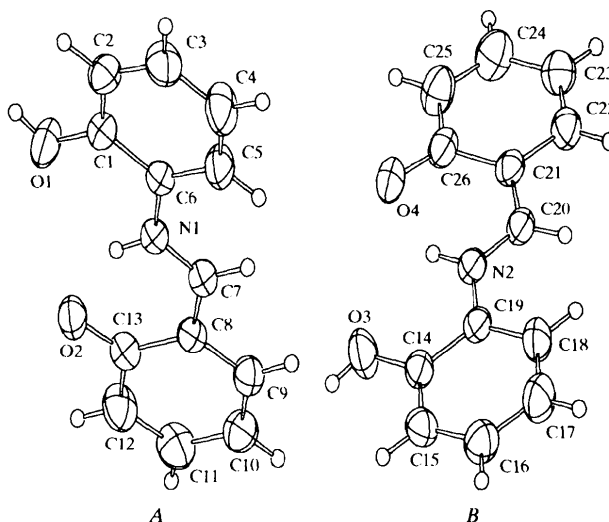

Fig. 1. *ORTEPII* (Johnson, 1976) view of the asymmetric unit of (I) with displacement ellipsoids shown at the 50% probability level.
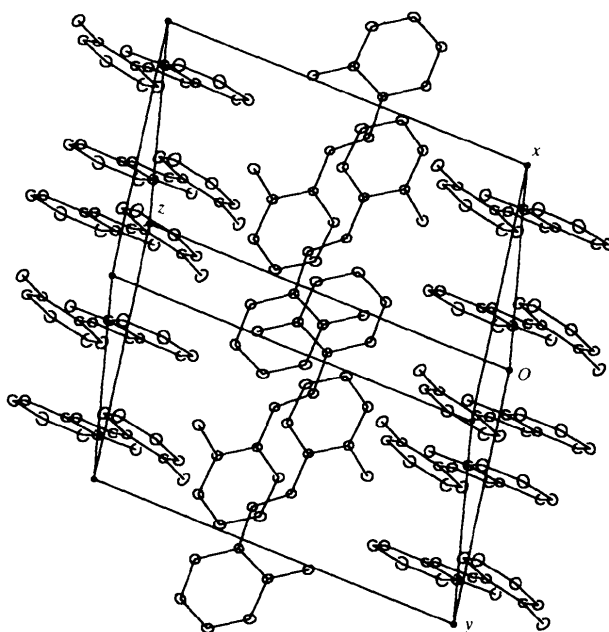

Fig. 2. The molecular packing in (I).

Experimental

N-p-acetophenylsalicylaldimine (SACPNH) was prepared by condensation of equimolar quantities of salicylaldehyde and 4-aminoacetophenone in refluxing ethanol. Compound (I) was

obtained from the reaction of 2-aminophenol (0.002 mol, 0.22 g) with a solution of SACPNH (0.002 mol, 0.48 g) in 40 ml of ethanol. The orange–red precipitate was separated and recrystallized in methylene chloride–*n*-hexane solution.

Crystal data

$C_{13}H_{11}NO_2$	Cu $K\alpha$ radiation
$M_r = 213.23$	$\lambda = 1.54180$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 9.034(2)$ Å	$\theta = 4$–$75°$
$b = 10.155(1)$ Å	$\mu = 0.758$ mm^{-1}
$c = 12.368(2)$ Å	$T = 293(2)$ K
$\alpha = 110.35(1)°$	Prism
$\beta = 89.90(2)°$	$0.42 \times 0.34 \times 0.20$ mm
$\gamma = 103.02(1)°$	Orange–red
$V = 1032.8(3)$ Å^3	
$Z = 4$	
$D_x = 1.371$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	3148 reflections with $I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.011$
Absorption correction: empirical (North *et al.*, 1968)	$\theta_{max} = 74.84°$
	$h = 0 \rightarrow 11$
	$k = -12 \rightarrow 12$
$T_{min} = 0.775$, $T_{max} = 0.859$	$l = -15 \rightarrow 15$
3863 measured reflections	3 standard reflections
3676 independent reflections	every 100 reflections intensity decay: <2%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.297$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.050$	$\Delta\rho_{min} = -0.294$ e Å^{-3}
$wR(F^2) = 0.125$	Extinction correction:
$S = 1.087$	*SHELXL*93 (Sheldrick, 1993)
3676 reflections	
312 parameters	Extinction coefficient:
H atoms: see text	0.0030(7)
$w = 1/[\sigma^2(F_o^2) + (0.0948P)^2]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	*International Tables for*
$(\Delta/\sigma)_{max} = 0.011$	*Crystallography* (Vol. C)

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

O1—C1	1.348(2)	C7—C8	1.416(2)
O2—C13	1.294(2)	C8—C9	1.415(2)
O3—C14	1.354(2)	C8—C13	1.432(2)
O4—C26	1.297(2)	C12—C13	1.415(2)
N1—C7	1.298(2)	C20—C21	1.410(2)
N1—C6	1.412(2)	C21—C22	1.410(2)
N2—C20	1.299(2)	C21—C26	1.438(2)
N2—C19	1.412(2)	C25—C26	1.413(2)
C7—N1—C6	127.06(12)	C12—C13—C8	116.40(14)
C20—N2—C19	127.34(12)	N2—C20—C21	123.33(13)
N1—C7—C8	122.99(13)	C22—C21—C26	120.20(14)
C9—C8—C13	120.76(13)	C25—C26—C21	116.51(15)
O1—C1—C6—N1	−2.5(2)	O3—C14—C19—N2	1.7(2)
C6—N1—C7—C8	179.4(1)	C19—N2—C20—C21	179.9(1)
N1—C7—C8—C13	−1.0(2)	N2—C20—C21—C26	0.8(2)
C7—C8—C13—O2	−3.5(2)	C20—C21—C26—O4	3.4(2)

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

D—H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1N$\cdots$O2	2.597(2)	145.1(1)
N2—H2N$\cdots$O4	2.595(2)	143.0(1)
O1—H1O$\cdots$O4^i	2.585(2)	161.1(1)
O3—H3O$\cdots$O2^{ii}	2.571(2)	162.2(1)

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

The structure was solved by direct methods and refined by full-matrix anisotropic least squares without any constraint. H atoms were located from the difference Fourier maps; their positions were then idealized and treated as riding, and their isotropic displacement parameters were refined.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4 Software*. Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995). Software used to prepare material for publication: *SHELXL*93.

References

Bregman, J., Leiserowitz, L. & Osaki, K. (1964). *J. Chem. Soc.* pp. 2086–2100.

Debaerdemaeker, T., Germain, G., Main, P., Refaat, L. S., Tate, C. & Woolfson, M. M. (1988). *MULTAN*88. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.

Elerman, Y., Elmali, A., Atakol, O. & Svoboda, I. (1995). *Acta Cryst.* C51, 2344–2346.

Elerman, Y., Elmali, A., Kendi, E., Ozbey, S. & Ertuzun, V. (1997). *Acta Cryst.* C53, 1158–1160.

Elerman, Y., Kabak, M., Elmali, A. & Svoboda, I. (1998). *Acta Cryst.* C54, 128–130.

Elmali, A. & Elerman, Y. (1997). *Acta Cryst.* C53, 791–793.

Enraf–Nonius (1989). *CAD-4 Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Garnovski, A. D., Nivorozhkin, A. L. & Minkin, V. I. (1993). *Coord. Chem. Rev.* 126, 1–65.

Hadjoudis, E., Vittorakis, M. & Moustakali-Mavridis, I. (1987). *Tetrahedron*, 43, 1345–1360.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Long, N. J. (1995). *Angew. Chem. Int. Ed. Engl.* 34, 21–46.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Xu, X., You, X., Sun, Z., Wang, X. & Liu, H. (1994). *Acta Cryst.* C50, 1169–1171.
Zsolnai, L. & Pritzkow, H. (1995). *ORTEP for a Silicon Graphics Computer*. University of Heidelberg, Germany.

1,4-Diformyl-*t*-5-methyl-*r*-2,*t*-3-diphenyl-piperazine-1,4-dicarbaldehyde

P. Laavanya, K. Panchanatheswaran, R. Murugadoss and R. Jeyaraman

Department of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India. E-mail: pan@bdu.ernet.in

(*Received 11 May 1998; accepted 15 September 1998*)

Abstract

A single-crystal X-ray diffraction study of the title compound ($C_{19}H_{20}N_2O_2$) confirms the chair conformation of the piperazine ring, with the methyl and phenyl groups in axial orientations.

Comment

The major highlight of this investigation is the presence of an alternate chair conformation of the piperazine ring of the title compound, (I), in which the phenyl and the methyl groups assume axial orientations. The nor-

(I)
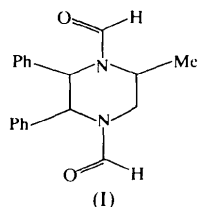
mal chair conformation with equatorial substituents is not preferred due to the steric interaction between the *N*-formyl and phenyl groups. The C5—C6 and C3—C2 bond distances, 1.519 (3) and 1.537 (3) Å, respectively, are in the range 1.515–1.535 Å reported for other piperazine derivatives (Sekido *et al.*, 1985; Okamato *et al.*, 1979, 1982; Sakurai *et al.*, 1977; Davis & Hassel, 1963). The bond angles around the C*sp*^{3} atoms in the piperazine ring [109.0 (2)–111.3 (2)°] indicate only slight distortion from the tetrahedral arrangement of groups around these atoms. The bond angles around N1 and N4 [116.6 (2)–122.2 (2)°] suggest *sp*^{2} character for these atoms, as in the case of similar piperazine derivatives (Sekido *et al.*, 1985; Okamato *et al.*, 1979; Sakurai *et al.*, 1977). The N1 and N4 atoms are at a dis-

tance of 0.554 (2) and −0.594 (2) Å, respectively, from the C2—C3—C5—C6 plane, indicating a chair conformation in which the two N atoms are unsymmetrically disposed. The axial orientations of the methyl and the two phenyl groups are evident from the torsion angles, N4—C5—C6—C9 76.9 (2), N1—C2—C3—C16 −78.0 (2) and N4—C3—C2—C10 −78.2 (2)°.
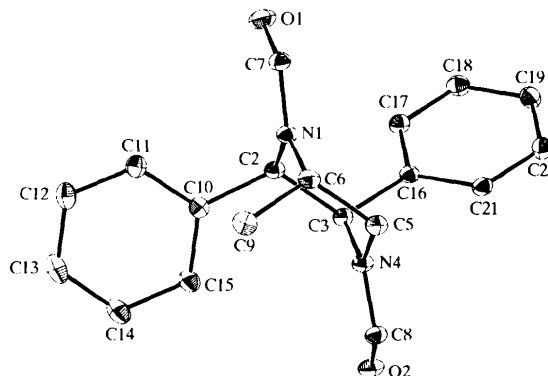

Fig. 1. *ZORTEP* (Zsolnai, 1997) plot of (I) showing 30% probability displacement ellipsoids. The H atoms are omitted for clarity.

Experimental

The title compound was obtained by the formylation of *t*-5-methyl-*r*-2,*t*-3-diphenylpiperazine by a mixture of acetic anhydride and 85% formic acid using benzene as solvent. The crude product isolated from the benzene layer was recrystallized using ethanol.

Crystal data

$C_{19}H_{20}N_2O_2$	Cu *K*α radiation
$M_r = 308.37$	λ = 1.54180 Å
Monoclinic	Cell parameters from 25
$P2_1/n$	reflections
a = 12.355 (3) Å	θ = 4.12–70.13°
b = 11.645 (3) Å	μ = 0.657 mm^{-1}
c = 12.750 (3) Å	*T* = 293 (2) K
β = 117.407 (16)°	Cubic
V = 1628.5 (7) Å^3	0.1 × 0.1 × 0.1 mm
Z = 4	Colourless
$D_x = 1.258$ Mg m^{-3}	
D_m not measured	

Data collection

Rigaku AFC-7*S* diffractometer	2382 reflections with $I > 2\sigma(I)$
ω–2θ scans	$R_{int} = 0.060$
Absorption correction:	$\theta_{max} = 70.13°$
ψ scans (North *et al.*, 1968)	*h* = 0 → 15
	k = 0 → 14
$T_{min} = 0.829$, $T_{max} = 0.936$	*l* = −15 → 13
3358 measured reflections	3 standard reflections
3021 independent reflections	every 150 reflections
	intensity decay: negligible