C9	0.74940 (15)	0.2224 (3)	0.17747 (12)	0.0440 (5)
C10	0.7363 (2)	0.3888 (3)	0.21507 (13)	0.0491 (6)
C11	0.6822 (2)	0.1682 (3)	0.09534 (12)	0.0480 (5)
C12	0.6960 (2)	−0.1214 (3)	0.02941 (13)	0.0523 (6)
C13	0.61755 (15)	−0.1349 (3)	0.06285 (12)	0.0457 (5)
C14	0.5603 (2)	−0.2909 (3)	0.06026 (13)	0.0525 (6)
C15	0.4956 (2)	−0.2662 (3)	0.09938 (13)	0.0504 (6)
C16	0.3713 (2)	−0.2886 (4)	0.1406 (2)	0.0694 (7)
C17	0.4874 (2)	−0.1002 (3)	0.13952 (13)	0.0489 (6)
C18	0.5429 (2)	0.0539 (3)	0.14271 (13)	0.0480 (6)
C19	0.60919 (14)	0.0310 (3)	0.10225 (12)	0.0438 (5)

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

O1—C5	1.363 (3)	C5—C10	1.390 (3)
O1—C1	1.415 (3)	C6—C7	1.392 (3)
O2—C6	1.371 (3)	C7—C8	1.377 (3)
O2—C2	1.421 (3)	C8—C9	1.383 (3)
O3—C7	1.366 (3)	C9—C10	1.374 (3)
O3—C3	1.422 (3)	C9—C11	1.512 (3)
O4—C12	1.400 (3)	C11—C19	1.506 (3)
O4—C4	1.424 (3)	C12—C13	1.479 (3)
O5—C12	1.423 (3)	C13—C19	1.369 (3)
O5—C11	1.441 (3)	C13—C14	1.395 (3)
O6—C15	1.380 (3)	C14—C15	1.360 (3)
O6—C16	1.424 (3)	C15—C17	1.375 (3)
O7—C17	1.373 (3)	C17—C18	1.366 (3)
O7—C16	1.427 (3)	C18—C19	1.398 (3)
C5—C6	1.386 (3)		
C5—O1—C1	117.8 (2)	O5—C11—C19	104.0 (2)
C6—O2—C2	115.3 (2)	O5—C11—C9	112.4 (2)
C7—O3—C3	117.6 (2)	C19—C11—C9	113.7 (2)
C12—O4—C4	113.9 (2)	O4—C12—O5	112.1 (2)
C12—O5—C11	111.1 (2)	O4—C12—C13	107.8 (2)
C15—O6—C16	104.9 (2)	O5—C12—C13	105.0 (2)
C17—O7—C16	104.9 (2)	C19—C13—C14	122.1 (2)
O1—C5—C6	115.7 (2)	C19—C13—C12	109.9 (2)
O1—C5—C10	124.3 (2)	C14—C13—C12	127.9 (2)
C6—C5—C10	120.0 (2)	C15—C14—C13	115.3 (2)
O2—C6—C5	119.3 (2)	C14—C15—C17	122.7 (2)
O2—C6—C7	121.4 (2)	C14—C15—O6	128.0 (2)
C5—C6—C7	119.1 (2)	C17—C15—O6	109.3 (2)
O3—C7—C8	124.4 (2)	O6—C16—O7	107.4 (2)
O3—C7—C6	114.8 (2)	C18—C17—O7	127.4 (2)
C8—C7—C6	120.8 (2)	C18—C17—C15	122.8 (2)
C7—C8—C9	119.5 (2)	O7—C17—C15	109.8 (2)
C10—C9—C8	120.4 (2)	C17—C18—C19	115.1 (2)
C10—C9—C11	119.3 (2)	C13—C19—C18	121.9 (2)
C8—C9—C11	120.2 (2)	C13—C19—C11	108.9 (2)
C9—C10—C5	120.1 (2)	C18—C19—C11	129.2 (2)

The unit-cell and intensity data were recorded at 140 K on a FAST area detector diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989) and processed using *ABSURD* (Karaulov, 1992); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). The structure was solved using *SHELXS*86 (Sheldrick, 1990) and refined using *SHELXL*93 (Sheldrick, 1993). The H atoms were included in idealized positions with $U_{\rm iso}$ values freely refined. The diagram was drawn with *SNOOPI* (Davies, 1983). Calculations were carried out on a 486DX2/66 personal computer. Material for publication was prepared using *SHELXL*93.

We thank the EPSRC for support of the X-ray Crystallography Service at UWC.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Darr, J. A., Drake, S. R., Hursthouse, M. B. & Malik, K. M. A. (1993). *Inorg. Chem.* **32**, 5704–5708.
Davies, K. (1983). *SNOOPI. Molecular Plotting Program.* Chemical Crystallography Laboratory, Univ. of Oxford, England.
Karaulov, A. I. (1992). *ABSURD. Program for FAST Data Processing.* Univ. of Wales, Cardiff, Wales.
Keay, B. A., Plaumann, H. P., Rajapaksa, D. & Rodrigo, R. (1983). *Can. J. Chem.* **61**, 1987–1995.
Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES.* Version 11 September, 1989. Distributed by Delft Instruments, Delft, The Netherlands.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Ward, R. S., Pelter, A., Galletti, G. C. & Qianrong, Li (1993). *J. Anal. Appl. Pyrolysis*, **27**, 187–197.

Acta Cryst. (1995). C**51**, 1893–1895

Salicylaldehyde Benzoyl Hydrazone

A. Lyubchova, A. Cossé-Barbi and J. P. Doucet

Institut de Topologie et Dynamique des Systèmes, CNRS-URA 34, Université Denis Diderot, 2 Place Jussieu, 75251 Paris CEDEX 05, France

F. Robert

Chimie des Métaux de Transition, CNRS-URA 419, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris CEDEX 05, France

J.-P. Souron and M. Quarton

Cristallochimie du Solide, CNRS-URA 1388, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris CEDEX 05, France

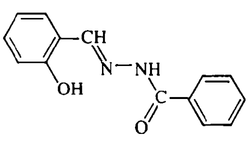
(*Received* 24 *March* 1994; *accepted* 2 *March* 1995)

Abstract

The crystallographic characterization of *N*-(2-hydroxybenzylideneamino)benzamide, $C_{14}H_{12}N_2O_2$, reveals quasi coplanarity of the whole molecular skeleton, localization of the double bonds in the central —C═N—N—C═O chain, which has an *E* configuration with respect to the double bond of the hydrazone bridge, and an amide *trans,s-cis* configuration around the single N—N bond. The molecules are held together by hydrogen bonds linking them into layers along the [100] direction.

Comment

Aroyl hydrazones are currently being investigated as orally active iron chelators for the treatment of iron overload, appearing in thalassemia or resulting from repeated blood transfusions (Bergsma, Cerami, Peterson & Graziano, 1976). Since the pioneering work of Ponka and co-workers (Ponka, Borova, Neuwirt, Fuchs & Necas, 1979; Ponka, Borova, Neuwirt & Fuchs, 1979; Ponka, Schulman & Wilzynska, 1982), salicylaldehyde benzoyl hydrazone (SBH) appears to be one of the most promising alternatives to desferrioxamine, the major drug used up to now which demands long and expensive treatment and is not free from side effects (Barry, Flynn, Letsky & Risdon, 1974; Pippard, Callender & Weatherall, 1978). The title compound, (I), has been investigated as part of a study of SBH and its complexes with p^6 and $3d$ metal ions.



(I)

All non-H atoms lie nearly in two planes (maximum deviation 0.06 Å): one plane corresponding to the phenyl ring of the benzoyl moiety, the other to the remaining part of the molecule. These two planes make a dihedral angle along the C(6)—C(7) bond of 23.61° in order to relieve steric interactions between atoms H(1) and H(21), which leads to a distance of 2.07 Å between these two atoms [O(1)···H(5) 2.476 Å]. The phenolic ring maintains coplanarity with the central chain, the distance between atoms H(14) and H(8) being 2.29 Å (Fig. 1).

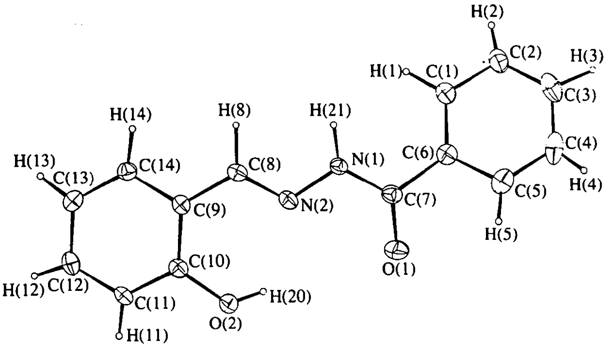


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the SBH molecule showing 50% probability displacement ellipsoids for non-H atoms.

The angle N(1)—C(7)—O(1) [123.1 (7)°] is significantly greater than C(6)—C(7)—O(1) [119.9 (7)°], possibly in order to relieve repulsion between lone pairs of electrons on atoms N(2) and O(1). The central part of the molecule, C(9)—C(8)—N(2)—N(1)—C(7)—C(6), adopts a completely extended conformation. The bond lengths C(8)—N(2) [1.291 (8) Å] and C(7)—O(1) [1.221 (7) Å] are typical of double bonds, so that the chain is likely to correspond to C(9)—C(8)=N(2)—N(1)—C(7)=O(1). A similar observation arises from values obtained for the related molecules pyridoxal isonicotinoyl hydrazone (Lyubchova, Cossé-Barbi, Doucet, Robert, Souron & Quarton, 1995) and *N*-pyridoxylidene-*N*′-picolinoyl hydrazine monohydrochloride monohydrate (Damiano, Musatti, Pelizzi & Predieri, 1978).

In the title structure, the molecules are held together by hydrogen bonds. Packing is determined by intermolecular hydrogen bonds linking the molecules into layers running along the [100] direction. It is interesting to note that there is an intermolecular hydrogen bond between the carbonyl O atom O(1) and the aromatic proton H(14), as well as extensive involvement of the phenolic OH group in hydrogen bonding, either intramolecularly [H(20)···N(2)] or intermolecularly [O(2)···H(21)] (Fig. 2).

The established crystal structure of SBH agrees well with the conformation proposed in solution on the basis of IR and NMR spectra (Colonna, Cossé-Barbi, Massat, Ben Abdelmoumene & Doucet, 1993).

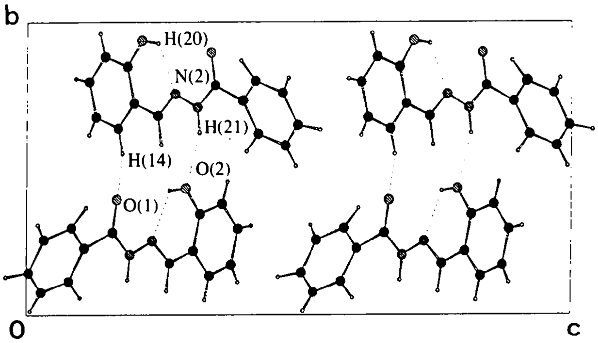


Fig. 2. Projection of the structure onto (100) showing the distribution of the hydrogen bonds.

Experimental

The title compound was prepared by dissolving benzoic acid hydrazide (10 mmol) in 60 ml of 50% ethanol. A solution of salicylaldehyde (10 mmol) in 5 ml of ethanol and 0.1 g of acetic acid was then added to the hydrazide solution with stirring. After 5 min a milky precipitate appeared. The mixture was placed on a steam bath for 30 min and 12 ml of ethanol was added until the precipitate dissolved, whereupon it was cooled to room temperature. The resulting crystal product was recrystallized from 80% ethanol as needle-like pale yellow crystals (yield 76%, m.p. 442 K). The product was characterized by microanalyses, IR and NMR spectroscopy, and mass spectrometry. Single crystals suitable for X-ray analysis were obtained under isostatic conditions [298 (1) K]. Their morphology was established by means of the double-circle optic goniometer Nedinsco and X-ray precision method. The picnometric density was measured at 293 K by immersion of about 1 g of powder in xylene (D = 0.861).

Crystal data

$C_{14}H_{12}N_2O_2$
$M_r = 240.26$
Orthorhombic
$Pc2_1n$
$a = 5.114\,(5)$ Å
$b = 10.896\,(3)$ Å
$c = 20.883\,(6)$ Å
$V = 1164\,(1)$ Å^3
$Z = 4$
$D_x = 1.370$ Mg m^{-3}
$D_m = 1.36\,(3)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 13\text{–}15°$
$\mu = 0.0875$ mm^{-1}
$T = 293$ K
Needle
0.50 × 0.17 × 0.10 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.967$, $T_{\max} = 0.984$
1242 measured reflections

1078 independent reflections
576 observed reflections $[I \geq 3\sigma(I)]$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 24$
3 standard reflections frequency: 60 min intensity decay: <1%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.033$
$S = 1.47$
576 reflections
164 parameters
Only H-atom U's refined
Unit weights applied

$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.05$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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	$U_{\rm eq}$
O(1)	0.208 (1)	0.3978 (4)	0.1644 (3)	0.0662
O(2)	0.7758 (9)	0.4377 (4)	0.2904 (2)	0.0526
N(1)	0.358 (1)	0.2099 (4)	0.1889 (2)	0.0395
N(2)	0.542 (1)	0.2570 (5)	0.2293 (2)	0.0425
C(1)	0.088 (1)	0.1188 (6)	0.0763 (3)	0.0491
C(2)	−0.066 (2)	0.0799 (7)	0.0263 (3)	0.0587
C(3)	−0.260 (2)	0.1490 (9)	0.0036 (3)	0.0630
C(4)	−0.321 (1)	0.2609 (8)	0.0315 (4)	0.0666
C(5)	−0.173 (1)	0.3022 (7)	0.0818 (3)	0.0574
C(6)	0.034 (1)	0.2319 (6)	0.1053 (3)	0.0468
C(7)	0.205 (1)	0.2868 (6)	0.1563 (3)	0.0460
C(8)	0.685 (1)	0.1814 (5)	0.2616 (3)	0.0391
C(9)	0.885 (1)	0.2234 (6)	0.3043 (3)	0.0389
C(10)	0.930 (1)	0.3496 (6)	0.3166 (3)	0.0433
C(11)	1.123 (1)	0.3833 (6)	0.3580 (3)	0.0477
C(12)	1.285 (1)	0.2991 (6)	0.3864 (3)	0.0517
C(13)	1.247 (1)	0.1757 (6)	0.3743 (3)	0.0498
C(14)	1.053 (1)	0.1381 (6)	0.3336 (3)	0.0462

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

O(1)—C(7)	1.221 (7)	O(2)—C(10)	1.356 (7)
N(1)—N(2)	1.365 (6)	N(1)—C(7)	1.332 (8)
N(2)—C(8)	1.291 (8)	C(1)—C(2)	1.375 (9)
C(1)—C(6)	1.400 (9)	C(2)—C(3)	1.33 (1)
C(3)—C(4)	1.39 (1)	C(4)—C(5)	1.37 (1)
C(5)—C(6)	1.397 (9)	C(6)—C(7)	1.502 (9)
C(8)—C(9)	1.432 (8)	C(9)—C(10)	1.418 (8)
C(9)—C(14)	1.406 (9)	C(10)—C(11)	1.363 (8)
C(11)—C(12)	1.371 (9)	C(12)—C(13)	1.381 (9)
C(13)—C(14)	1.367 (9)		
C(7)—N(1)—N(2)	118.9 (5)	C(8)—N(2)—N(1)	118.2 (5)
C(6)—C(1)—C(2)	119.2 (7)	C(3)—C(2)—C(1)	121.5 (8)
C(4)—C(3)—C(2)	121.0 (8)	C(5)—C(4)—C(3)	119.0 (8)
C(6)—C(5)—C(4)	120.6 (7)	C(5)—C(6)—C(1)	118.6 (7)
C(7)—C(6)—C(1)	122.9 (6)	C(7)—C(6)—C(5)	118.2 (6)
N(1)—C(7)—O(1)	123.1 (7)	C(6)—C(7)—O(1)	119.9 (7)
C(6)—C(7)—N(1)	116.9 (6)	C(9)—C(8)—N(2)	121.7 (6)
C(10)—C(9)—C(8)	122.6 (6)	C(14)—C(9)—C(8)	119.8 (6)
C(14)—C(9)—C(10)	117.6 (6)	C(9)—C(10)—O(2)	121.3 (6)
C(11)—C(10)—O(2)	119.1 (6)	C(11)—C(10)—C(9)	119.5 (6)
C(12)—C(11)—C(10)	122.1 (6)	C(13)—C(12)—C(11)	119.1 (6)
C(14)—C(13)—C(12)	120.5 (7)	C(13)—C(14)—C(9)	121.0 (6)

A scan width of $(0.8 + 0.345\tan\theta)°$ and scan rate of 1° min^{-1} were used with background counts for 5 s on each side of every scan. The positions of the non-H atoms were obtained by direct methods using *SHELXS*86 (Sheldrick, 1985) and H atoms were found in difference Fourier maps. Non-H atoms were refined with anisotropic displacement. Isotropic displacement parameters of H atoms were fixed at $U = 0.078$ Å^2, the mean value obtained during a precedent refinement cycle using *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). The largest peak on the final difference Fourier map was situated 0.76 Å from atom C(13), along a direction perpendicular to the phenolic cycle.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1117). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Barry, M., Flynn, D. M., Letsky, E. A. & Risdon, R. A. (1974). *Br. Med. J.* **1**, 16–22.

Bergsma, D., Cerami, A., Peterson, C. M. & Graziano, J. H. (1976). In *Iron Metabolism and Thalassemia, Birth Defects, Ser.* 12. New York: Alan R. Liss.

Colonna, C., Cossé-Barbi, A., Massat, A., Ben Abdelmoumene, R. & Doucet, J. P. (1993). *Bull. Soc. Chim. Belg.* **102**, 411–430.

Damiano, P., Musatti, A., Pelizzi, C. & Predieri, G. (1978). *Cryst. Struct. Commun.* **7**, 751–755.

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

Lyubchova, A., Cossé-Barbi, A., Doucet, J. P., Robert, F., Souron, J.-P. & Quarton, M. (1995). In preparation.

Pippard, M. J., Callender, S. T. & Weatherall, D. J. (1978). *Clin. Sci. Mol. Med.* **54**, 99–106.

Ponka, P., Borova, J., Neuwirt, J. & Fuchs, O. (1979). *FEBS Lett.* **97**, 317–321.

Ponka, P., Borova, J., Neuwirt, J., Fuchs, O. & Necas, E. (1979). *Biochim. Biophys. Acta*, **586**, 287–297.

Ponka, P., Schulman, H. M. & Wilzynska, A. (1982). *Biochim. Biophys. Acta*, **718**, 151–156.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.

Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide.* Chemical Crystallography Laboratory, Univ. of Oxford, England.