$S = 1.054$
3056 reflections
249 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0610P)^2 + 0.3308P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

Table 1. *Selected bond lengths (Å)*

O1—C6	1.215 (2)	O4—N1	1.205 (2)
O2—C5	1.450 (2)	N1—C1	1.519 (2)
O2—C4	1.452 (2)	C4—C5	1.470 (2)
O3—N1	1.202 (2)	C9—C10	1.321 (3)

The data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω. The crystal-to-detector distance was 4 cm and the detector swing angle was −35°. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the duplicate reflections; it was found to be negligible. The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference Fourier map and refined isotropically.

Data collection: *SMART* (Siemens, 1996*c*). Cell refinement: *SAINT* (Siemens, 1996*a*). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Siemens, 1996*b*). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1220). Services for accessing these data are described at the back of the journal.

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2-(2-Hydroxybenzylidene)-1-(2-picoloyl)hydrazine Hemihydrate

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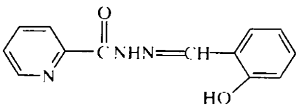
Abstract

In the title compound [2-hydroxybenzaldehyde 2-pyridylcarbonylhydrazone hemihydrate, $C_{13}H_{11}N_3O_2 . 0.5H_2O$ or (1).0.5H_2O], molecules of (1) are linked pairwise through intermolecular N—H···N hydrogen bonds. These pairs alternate with hydrogen-bonded water molecules to form one-dimensional chains.

Comment

Compared to simple hydrazone Schiff bases, acyl, aroyl and heteroaroyl Schiff bases have an additional O-donor atom from the carbonyl group, whose presence introduces a wider range of properties (Dutta & Hossain, 1985). These compounds may therefore function as polydentate ligands and some reports of their complexes have appeared (Dutta & Sarkar, 1981; Aggarwal *et al.*, 1981; Dutta & Das, 1985).

Molecules of (1) are essentially planar [r.m.s. deviation from the least-squares mean plane is only 0.051 (7) Å]. The O1···N1 separation of 2.669 (8) Å, which is less than the sum of the corresponding van der Waals radius sum (2.85 Å), suggests a possible intramolecular hydrogen bond, as does the O1—H1···N1 bond angle of 144.9 (5)°. Molecules of (1) are linked into pairs by intermolecular N2—H2···N3^i hydrogen bonds (Fig. 1) [N2···N3^i 3.116 (5) Å and



(1)

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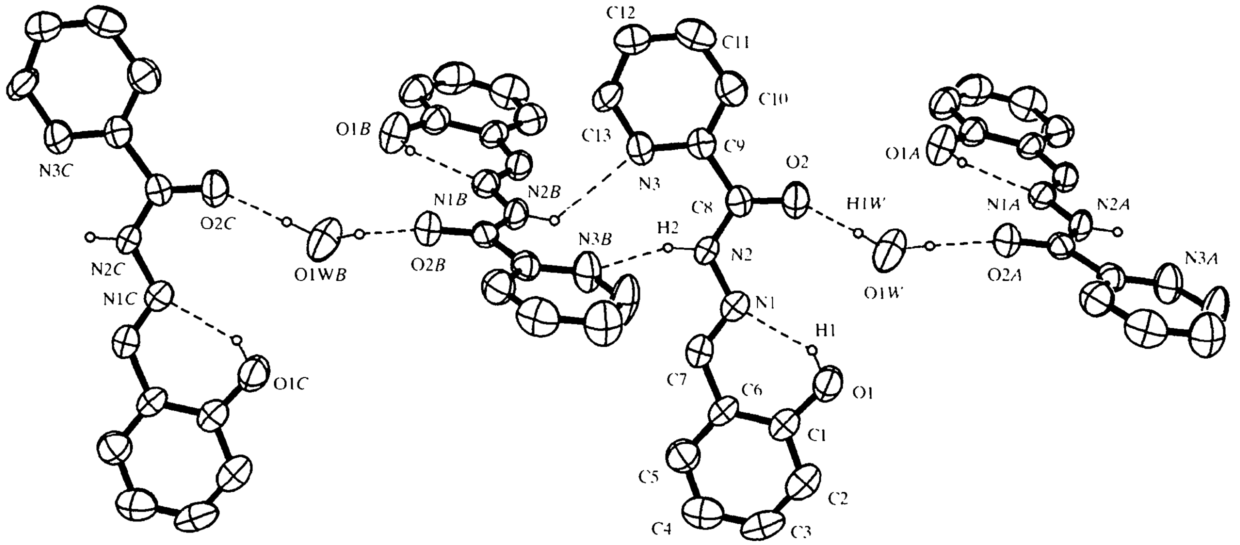

Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are shown at the 30% probability level. H atoms not involved in hydrogen bonding have been omitted for clarity.

N2—H2···N3^i 128°; symmetry code: (i) $-x$, y, $\frac{1}{2}-z$]. These pairs alternate with water molecules to form one-dimensional chains through O1*W*—H1*W*···O2 hydrogen bonds [O1*W*···O2 2.843 (4) Å and O1*W*—H1*W*···O2 176 (6)°]. The water molecules (O1*W*) lie on crystallographic twofold axes.

Experimental

The title compound was synthesized by refluxing an equimolar mixture of 2-picoloylhydrazine and salicylaldehyde in ethanol for 1 h (Dutta & Sarkar, 1981). Single crystals suitable for X-ray analysis were obtained from ethanol.

Crystal data

$C_{13}H_{11}N_3O_2.0.5H_2O$
$M_r = 250.26$
Orthorhombic
Pbcn
$a = 11.800\,(2)$ Å
$b = 16.538\,(4)$ Å
$c = 12.565\,(3)$ Å
$V = 2452.0\,(9)$ Å^3
$Z = 8$
$D_x = 1.356$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 17 reflections
$\theta = 4.89$–$8.14°$
$\mu = 0.097$ mm^{-1}
$T = 295\,(2)$ K
Hexagonal prism
0.50 × 0.40 × 0.40 mm
Pale yellow

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2351 measured reflections
2060 independent reflections
1124 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$

$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 11$
$k = -19 \rightarrow 0$
$l = 0 \rightarrow 14$
3 standard reflections every 97 reflections
random variation: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.227$
$S = 1.083$
2060 reflections
172 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.11P)^2 + 0.18P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C1	1.358 (5)	N2—C8	1.335 (5)
O2—C8	1.235 (4)	C6—C7	1.444 (6)
N1—C7	1.284 (5)	C8—C9	1.504 (6)
N1—N2	1.390 (4)		
C7—N1—N2	116.2 (3)	O2—C8—N2	124.1 (4)
C8—N2—N1	120.9 (3)	O2—C8—C9	121.6 (4)
N1—C7—C6	121.3 (4)	N2—C8—C9	114.2 (3)

The title structure was solved by direct methods and refined by full-matrix least squares. All the non-H atoms were refined anisotropically. The water H1*W* atom was located in a difference Fourier map and thereafter refined isotropically. Other H atoms were placed in geometrically calculated positions (C—H 0.93 and N—H 0.86 Å) with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom).

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Siemens, 1995). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1204). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1929–1934

Investigation of Three Stilbene Derivatives by X-ray Crystallography and NMR Spectroscopy

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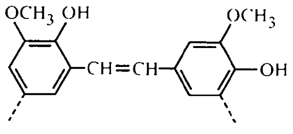
Abstract

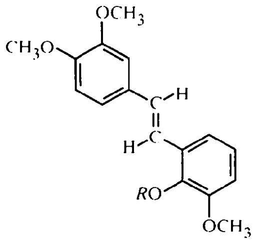
Crystal structure determinations demonstrate unambiguously the steric assignments of (*Z*)-2-hydroxy-3,3′,4′-trimethoxystilbene ($C_{17}H_{18}O_4$), (*E*)-2-hydroxy-3,3′,4′-trimethoxystilbene ($C_{17}H_{18}O_4$) and (*E*)-2-acetoxy-3,3′,4′-trimethoxystilbene ($C_{19}H_{20}O_5$). ^{13}C NMR data and UV data for the compounds are also reported. The steric assignments of structurally related compounds described in the literature are discussed on the basis of the crystallographic and spectral results.

Comment

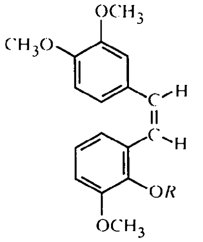
Stilbenes of type (1) have been detected in spent liquors from alkaline pulping (Gierer & Lindeberg, 1980; Niemelä, 1990; see also Miller & Schuerch, 1968). Experiments with lignin model compounds suggest that such stilbenes originate from structural elements in lignin of the phenylcoumaran type (Adler *et al.*, 1964; Yoon *et al.*, 1981). Conversion of such structural elements to stilbenes of type (1) also occurs under acid conditions (Li & Lundquist, 1998). Model experiments carried out by Lee *et al.* (1990) indicate that stilbenes of type (1) are formed on mechanical pulping. (*E*)-2-Hydroxy-3,3′,4′-trimethoxystilbene, (2*a*), and (*Z*)-2-hydroxy-3,3′,4′-trimethoxystilbene, (3*a*), are model compounds representative of lignin degradation products of type (1). To obtain unambiguous proof of the steric assignments of these stilbenes, crystal structure determinations of their acetate derivatives [*i.e.* compounds (2*b*) and (3*b*)] were carried out (Li *et al.*, 1996). The crystal structures of (2*b*) and the non-derivatized compounds [(2*a*) and (3*a*)] are described in this paper. The crystal structure determinations of (2*a*), (3*a*), (2*b*) and (3*b*) together with previously published NMR data (Li *et al.*, 1996; Li & Lundquist, 1998) and ^{13}C NMR and UV data reported in this paper provide a basis for the steric assignment of stilbenes of type (1). From the results of the studies of the stereochemistry of (2) and (3), it can be concluded that the *Z* form (3*b*) has incorrectly been assigned as the *E* form in two papers (Gierer *et al.*, 1974; Lee *et al.*, 1990).



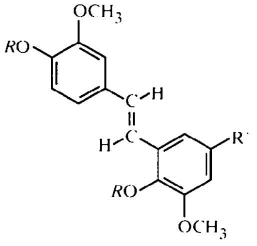
(1)

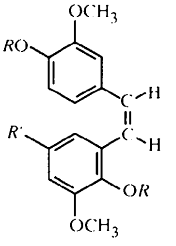


(2*a*) R = H
(2*b*) R = $\mathrm{COCH_3}$



(3*a*) R = H
(3*b*) R = $\mathrm{COCH_3}$





(4*a*) $R = R'$ = H
(4*b*) $R = \mathrm{COCH_3}, R'$ = H
(6*a*) $R = \mathrm{H}, R' = \mathrm{CH_3}$
(6*b*) $R = \mathrm{COCH_3}, R' = \mathrm{CH_3}$
(8*a*) $R = \mathrm{H}, R' = \mathrm{CH_2CH_2CH_2OH}$
(8*b*) $R = \mathrm{COCH_3}, R' = \mathrm{CH_2CH_2CH_2OH}$

(5*a*) $R = R'$ = H
(5*b*) $R = \mathrm{COCH_3}, R'$ = H
(7*a*) $R = \mathrm{H}, R' = \mathrm{CH_3}$
(7*b*) $R = \mathrm{COCH_3}, R' = \mathrm{CH_3}$

Both the *E* form (4*a*) and the *Z* form (5*a*) of a stilbene of type (1) have been detected in a kraft pulping liquor (Gierer & Lindeberg, 1980). The steric