(I), was obtained from column chromatography [m.p. 404 K, 3.2 g (74%) yield] and recrystallized from ethyl acetate.

Crystal data

$C_{18}H_{19}NO_2S_2$	Mo $K\alpha$ radiation
$M_r = 345.49$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 25
$Pbca$	reflections
$a = 9.202\,(1)$ Å	$\theta = 9–11°$
$b = 18.870\,(3)$ Å	$\mu = 0.324$ mm^{-1}
$c = 19.138\,(2)$ Å	$T = 298$ K
$V = 3323.2\,(7)$ Å^3	Block
$Z = 8$	$0.30 \times 0.25 \times 0.20$ mm
$D_x = 1.381$ Mg m^{-3}	Yellow
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.023$
diffractometer	$\theta_{max} = 26.3°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 11$
Absorption correction:	$k = 0 \rightarrow 23$
empirical via ψ scans	$l = 0 \rightarrow 23$
($MolEN$; Fair, 1990)	3 standard reflections
$T_{min} = 0.910$, $T_{max} = 0.940$	every 250 reflections
3816 measured reflections	frequency: 120 min
3363 independent reflections	intensity decay: 1%
2922 reflections with	
$F > 2\sigma(F)$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.01$
$R = 0.038$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
$wR = 0.048$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
$S = 1.22$	Extinction correction: none
2922 reflections	Scattering factors from
256 parameters	$International\ Tables\ for$
H atoms: see text	$X\text{-}ray\ Crystallography$
$w = 1/[\sigma(F)^2 + (0.02F)^2$	(Vol. IV)
$+ 1.0]$	

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

S1—C1	1.856 (2)	C3—C4	1.495 (3)
S1—C10	1.815 (2)	C4—C4a	1.449 (3)
S2—C1	1.832 (2)	C4a—C5a	1.439 (3)
S2—C11	1.799 (2)	C4a—C9a	1.384 (2)
O1—C4	1.224 (2)		
C1—S1—C10	97.89 (9)	C3—C4—C4a	114.6 (2)
C1—S2—C11	95.04 (9)	C1—C9a—C4a	122.8 (2)
S1—C1—S2	107.37 (9)	S1—C10—C11	109.0 (2)
S2—C1—C2	112.1 (1)	S2—C11—C10	107.2 (1)
C2—C1—C9a	108.6 (1)	C4—C4a—C9a	124.5 (2)
C1—C2—C3	114.3 (2)	C8a—N9—C9a	108.1 (1)
C2—C3—C4	115.1 (2)		

Most of the H-atom positions were located by difference synthesis and refined isotropically. The remaining ones were positioned geometrically and a riding model was used during the refinement process.

Data collection: *MolEN* (Fair, 1990). Cell refinement: *MolEN*. Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN*.

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4-(2,5-Di-*tert*-butylphenylnitrilomethylidyne)-2-methoxyphenol

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Abstract

The title compound, $C_{22}H_{29}NO_2$, is a monodentate Schiff base. There are two independent molecules in the asymmetric unit. In each molecule the two planar phenyl rings bridged by a C=N imino moiety are nearly perpendicular to one another [79.80 (4) and 81.14 (4)°]. Each molecule contains intramolecular (O—H···O) and intermolecular (O—H···N) hydrogen bonds.

Comment

Schiff bases and their transition metal complexes have been extensively studied during the last decade.
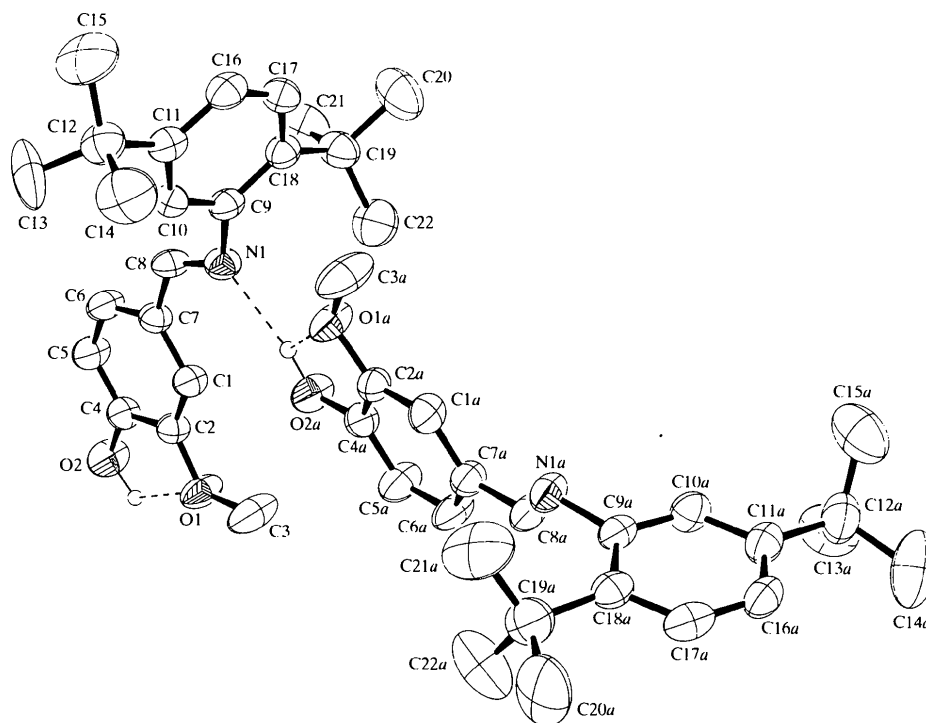
Fig. 1. The molecular structure (ORTEPII; Johnson, 1976) of the title compound, showing the atom labelling scheme and the 50% probability level displacement ellipsoids for the non-H atoms. All H atoms are omitted except for that on O2 (H2O).

Among these bases, Schiff base compounds show photochromism and thermochromism in the solid state by proton transfer from the hydroxy-O atom to the imine N atom (Moustakali-Mavridis et al., 1978; Hadjoudis et al., 1987; Xu et al., 1994). Our structural investigations into Schiff bases (Elerman et al., 1991, 1992, 1994, 1995, 1997, 1998; Elerman & Elmali, 1998; Elmali et al., 1995; Elmali & Elerman, 1997, 1998; Elmali, Elerman & Zeyrek, 1998; Elmali, Elerman & Kendi, 1998; Elmali, Elerman, Svoboda & Fuess, 1998) led us to examine the structure of the title compound, (I).

(I)
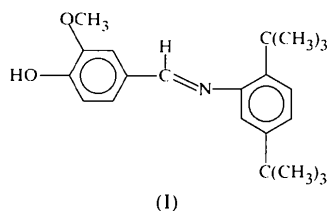
Ab initio calculations on benzylideneaniline and related molecules have shown that rotations about the Ph—N bond of up to 45° from a planar conformation stabilize the molecule, while rotations about the Ph—C bond destabilize it. The most stable free-molecule conformation is non-planar (Hadjoudis et al., 1987). The title compound has two crystallographically indepen-

dent molecules in the asymmetric unit. The two planar phenyl rings bridged by the C=N imino moiety in the two crystallographically independent molecules, however, are inclined at an angle of 79.80 (4) and 81.14 (4)°, respectively, while in the similar compound, N-p-tolyl-vanillaldimine, the planar phenyl rings were reported to be inclined at an angle of 40.26 (9)° (Kaitner & Pavlović, 1995).

The crystal structure is stabilized by intramolecular and intermolecular hydrogen bonding. Intramolecular hydrogen bonds occur between hydroxy-O1 and methoxy-O2 [2.641 (2) Å], and hydroxy-O1a and methoxy-O2a [2.644 (1) Å] atoms. There is an intermolecular O—H···N hydrogen bond linking the neighbouring molecules into infinite chains along the b axis (Table 2). Apart from the intramolecular and intermolecular hydrogen bonds, there are also intermolecular C—H···O close contacts. Close C1—H···O2a and C1a—H···O2 contacts of 3.200 (2) and 3.223 (2) Å can be regarded as weak electrostatic attractions (Steiner, 1996).

Experimental

The title compound was obtained from the reaction of vanillin (0.01 mol) with a solution of 2,5-di-tert-butylaniline (0.01 mol) in 50 ml of ethanol. The precipitate which separated from the solution was recrystallized for 6 h from 0.2 g of Schiff base in 30 ml of acetonitrile solution.

Crystal data

C$_{22}$H$_{29}$NO$_2$
$M_r = 339.46$
Triclinic
$P\bar{1}$
$a = 10.2979\,(8)$ Å
$b = 13.1101\,(11)$ Å
$c = 16.7038\,(13)$ Å
$\alpha = 78.0476\,(6)°$
$\beta = 71.3989\,(6)°$
$\gamma = 79.6493\,(7)°$
$V = 2075.2\,(3)$ Å^3
$Z = 4$
$D_x = 1.087$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25
    reflections
$\theta = 10.2–24.3°$
$\mu = 0.069$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.45 \times 0.35 \times 0.30$ mm
Colourless

Data collection

Enraf–Nonius CAD-4
    diffractometer
$\theta/2\theta$ scans
Absorption correction: none
7711 measured reflections
7711 independent reflections
4842 reflections with
    $I > 2\sigma(I)$

$\theta_{max} = 25.49°$
$h = -11 \rightarrow 12$
$k = -15 \rightarrow 15$
$l = 0 \rightarrow 20$
3 standard reflections
    frequency: 120 min
    intensity decay: 3.4%

Refinement

Refinement on F^2
$R(F) = 0.061$
$wR(F^2) = 0.162$
$S = 0.962$
7711 reflections
457 parameters
H atoms treated by a
    mixture of independent
    and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.3321P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.007$
$\Delta\rho_{max} = 0.172$ e Å^{-3}
$\Delta\rho_{min} = -0.205$ e Å^{-3}
Extinction correction: none
Scattering factors from
    International Tables for Crystallography (Vol. C)

The structure was solved by direct phase determination. The parameters of the complete structure could be refined by full-matrix anisotropic least squares. All phenyl rings were refined without any constraints. Values of distances and angles in the rings show no significant differences from those of an ideal benzene ring. H atoms bonded to C atoms were refined using a riding model and H-atom displacement parameters were restricted to be $1.2U_{eq}$ of the parent atom. The H2O(O2) atom was located in the difference Fourier maps calculated at the end of the refinement process as a small, positive electron density.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *MolEN* (Fair, 1990). Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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

C2—O1	1.364 (2)	C2a—O1a	1.363 (2)
C3—O1	1.416 (2)	C3a—O1a	1.409 (2)
C4—O2	1.363 (2)	C4a—O2a	1.366 (2)
C8—N1	1.268 (2)	C8a—N1a	1.271 (2)
C9—N1	1.426 (2)	C9a—N1a	1.436 (2)
O1—C2—C1	126.39 (12)	O1a—C2a—C1a	126.46 (12)
O1—C2—C4	113.54 (11)	O1a—C2a—C4a	113.59 (11)
O2—C4—C5	119.79 (12)	O2a—C4a—C5a	119.04 (12)
O2—C4—C2	120.56 (12)	O2a—C4a—C2a	120.94 (12)
N1—C8—C7	125.86 (12)	N1a—C8a—C7a	126.21 (12)
C10—C9—N1	116.49 (12)	C10a—C9a—N1a	116.74 (11)
C18—C9—N1	122.80 (12)	C18a—C9a—N1a	122.42 (12)
C2—O1—C3	117.51 (11)	C2a—O1a—C3a	117.29 (11)
C8—N1—C9	117.20 (11)	C8a—N1a—C9a	116.91 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2O···O1	0.985 (17)	2.312 (18)	2.641 (2)	98 (1)
O2a—H2Oa···O1a	0.960 (16)	2.111 (17)	2.644 (1)	106 (1)
O2a—H2Oa···N1	0.960 (16)	2.112 (16)	2.962 (1)	147 (2)
O2—H2O···N1a^i	0.985 (17)	2.069 (16)	2.979 (2)	153 (2)
C1—H1···O2a	0.930 (2)	2.284 (2)	3.200 (2)	169 (1)
C1a—H1a···O2^{ii}	0.930 (2)	2.333 (2)	3.223 (2)	160 (1)

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

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2-(2-Pyrrolyl)-1,3-benzothiazole

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Abstract

The title compound, $C_{11}H_8N_2S$, already known from the literature, was prepared and studied by X-ray diffraction. The five-membered heterocyclic ring is coplanar with its fused benzene ring. However, the molecule itself is non-planar, with the dihedral angle between the planes of the 2-benzothiazolyl and pyrrolyl groups being 17.3 (7)°. The molecules related by the twofold rotation axis are connected in pairs by N—H···N hydrogen bonds of 3.032 (9) Å.

Comment

Organic luminescent materials are widely used in the basic as well as applied research fields and various kinds of luminescent compounds are now known. Among this group of compounds are benzothiazole derivatives, whose importance as substances used as fluorescent brighteners (Allen, 1971) and for fluorometric measurements (Akiyama *et al.*, 1987) has led us to study the spectral characteristics of some aryl- and hetero-aryl-substituted benzothiazoles (Tralić-Kulenović *et al.*, 1993). 2-(2-Pyrrolyl)benzothiazole (Brown, 1962) exhibited a relatively large fluorescence quantum efficiency and it was therefore of interest to find out more about the structure of this compound, (I).

(I)
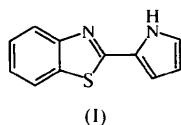
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The bond distances in both five-membered heterocyclic rings are consistent with those usually found in the literature (Potenza & Mastropaolo, 1974; Rudd & Barany, 1984). The benzene ring and its fused thiazolyl ring are coplanar. The bond S—C11 [1.739 (3) Å] is shorter than S—C5 [1.754 (3) Å], due to the fact that C5 is sp^2 hybridized, whereas C11 is part of the aromatic ring (Yeap *et al.*, 1991). Therefore, the molecular structure is not planar; the dihedral angle between the planes of the 2-benzothiazolyl and pyrrolyl groups is 17.3 (7)°. The deviation from coplanarity is significant; the torsion angles N1—C1—C5—N2, N1—C1—C5—S, C4—C1—C5—N2 and C4—C1—C5—S are 11.1 (4), −172.4 (2), −159.6 (3) and 16.9 (5)°, respectively.

The molecules, related by the twofold rotation axis, are connected in pairs by two hydrogen bonds [NH···N 3.032 (9), H···N 2.169 (7) Å and N—H···N 166.0 (7)°].
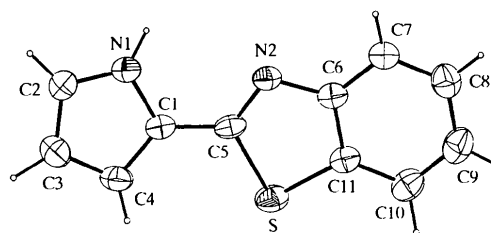

Fig. 1. View of the title molecule with the atom-labelling scheme for the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was prepared from aminothiophenole and the required heteroaldehyde according to the method of Bogert & Stull (1935). Good quality crystals for X-ray diffraction analysis were obtained by slow evaporation from a dimethylformamide solution.

Crystal data

$C_{11}H_8N_2S$	Mo $K\alpha$ radiation
$M_r = 200.25$	$\lambda = 0.71073$ Å
Tetragonal	Cell parameters from 32
$P4_32_12$	reflections
$a = 8.0916 (9)$ Å	$\theta = 7.8–13.1°$
$c = 30.078 (4)$ Å	$\mu = 0.285$ mm^{-1}
$V = 1969.3 (4)$ Å^3	$T = 293 (2)$ K
$Z = 8$	Bipyramid
$D_x = 1.351$ Mg m^{-3}	$0.135 \times 0.120 \times 0.113$ mm
$D_m = 1.3$ Mg m^{-3}	Bronze
D_m measured by flotation in benzene/CCl$_4$	

Data collection

Philips PW1100 updated by	$R_{int} = 0.050$
Stoe diffractometer	$\theta_{max} = 28.99°$