

Acta Cryst. (1999). C55, 1707–1710

Four *N*-(2-hydroxybenzylidene)aniline derivatives†

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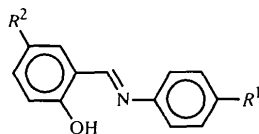
(Received 10 March 1999; accepted 17 June 1999)

Abstract

The molecular structures of *N*-(2-hydroxybenzylidene)-4-fluoroaniline, C₁₃H₁₀FNO, *N*-(2-hydroxybenzylidene)-4-trifluoromethoxyaniline, C₁₄H₁₀F₃NO₂, *N*-(2-hydroxy-5-chlorobenzylidene)-4-chloroaniline, C₁₃H₉Cl₂NO, and *N*-(2-hydroxybenzylidene)-4-nitroaniline, C₁₃H₁₀N₂O₃, have been determined. In each case, the conformations are such that the hydroxy group is aligned towards the N atom facilitating a strong intramolecular hydrogen bond.

Comment

Salicylideneanilines have proved popular ligands for many years. Although structures have been reported for a number of their complexes, rather few of these ligands have been structurally characterized by X-ray diffraction techniques. The structures of *N*-(2-hydroxybenzylidene)-4-methylaniline (Aldoshin *et al.*, 1982) and *N*-(2-hydroxybenzylidene)-perfluoroaniline (Lindeman *et al.*, 1981) were reported some time ago; we now report structures of four further ligands of this type, *N*-(2-hydroxybenzylidene)-4-fluoroaniline, (1), *N*-(2-hydroxybenzylidene)-4-trifluoromethoxyaniline, (2), *N*-(2-hydroxy-5-chlorobenzylidene)-4-chloroaniline, (3), and *N*-(2-hydroxybenzylidene)-4-nitroaniline, (4).



- (1) R¹ = F; R² = H
 (2) R¹ = OCF₃; R² = H
 (3) R¹, R⁴ = Cl
 (4) R² = NO₂; R² = H

For all four structures the presence of a strong intramolecular O—H...N hydrogen bond is unequivocally established by locating the hydroxy-H atom and the C5—O1—H1A...N1 geometry. The C5—O1—H1A

† Systematic names: 2-(4-fluorophenyliminomethyl)phenol, 2-(4-trifluoromethoxyphenyliminomethyl)phenol, 5-chloro-2-(4-chlorophenyliminomethyl)phenol and 2-(4-nitrophenyliminomethyl)phenol.

angles are in the range 100 (3) to 112 (2)°, the O1—H1A distances are between 0.83 (3) and 1.02 (6) Å and the H1A...N1 distances are in the range 1.62 (7) to 1.87 (3) Å (Table 1). The hydrogen bonds are also evidenced by the orientation in all cases of the C7=N1 bond to be in the plane of the C1—C6 ring with the minimum O1...N1 distances facilitated by the geometry (Figs. 1 to 4). The O1...N1 distances are indicative of a strong hydrogen bond, but are a function of the molecular geometry. The planar arrangement is to be

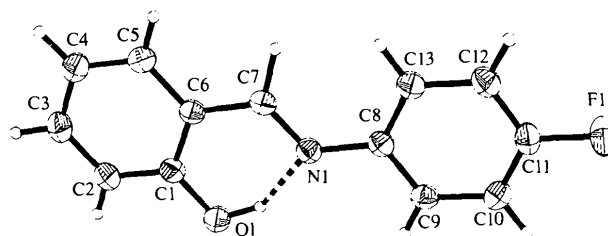


Fig. 1. The molecular structure of (1) showing the atom-numbering scheme and 30% displacement ellipsoids. The intramolecular hydrogen bonds are shown as dashed lines.

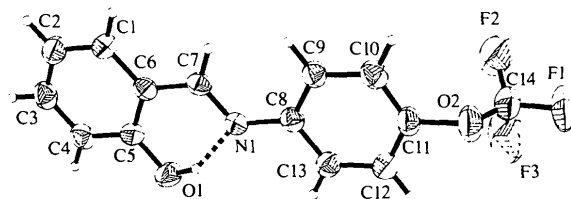


Fig. 2. The molecular structure of (2) showing the atom-numbering scheme and 30% displacement ellipsoids. The intramolecular hydrogen bonds are shown as dashed lines.

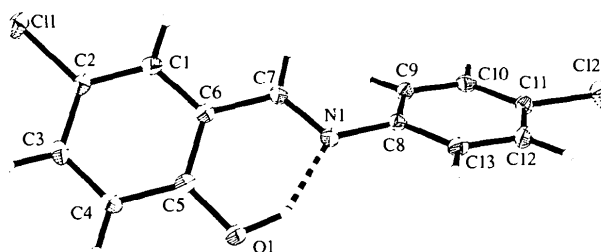


Fig. 3. The molecular structure of (3) showing the atom-numbering scheme and 30% displacement ellipsoids. The intramolecular hydrogen bonds are shown as dashed lines.

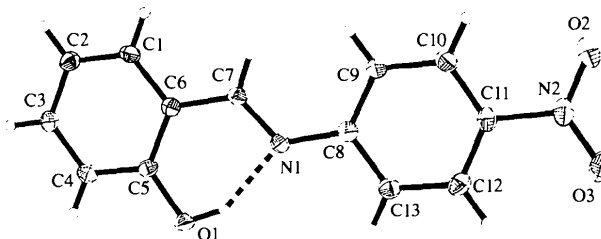


Fig. 4. The molecular structure of (4) showing the atom-numbering scheme and 30% displacement ellipsoids. The intramolecular hydrogen bonds are shown as dashed lines.

expected as a result of π orbital interactions. However, the opposite planar orientation with the ring and the C7=N1 bond rotated 180° with respect to each other, which would still allow π -bond interaction without the hydrogen bond, is not observed for any reported structure of this type. This may be a result of the mechanism of formation allowing only one conformation.

Compounds (1), (2) and (4) are essentially planar with interplanar angles between the rings of 2.17 (10), 3.1 (2) and 3.16 (14)°, respectively, similar to that found for the 4-methyl derivative (6.47°; Aldoshin *et al.*, 1982). By contrast the interplanar ring angle of (3) is 44.54 (6)°, comparable with those of the perfluoroaniline derivative (Lindeman *et al.*, 1981) which was studied over a range of temperatures and found to have two different forms with interplanar angles of 44.86 and 44.45° for one form and 40.06° for the second form.

The packing arrangements for the halogen-substituted compounds give rise to clearly defined channels of halogen atoms. The chloro-substituted derivative shows a typical stacking arrangement (Fig. 5) with molecules aligned along the *b* axis with 2.57 Å (*b*/2) interplanar distance between the molecules, the Cl atoms form channels perpendicular to the *a* axis.

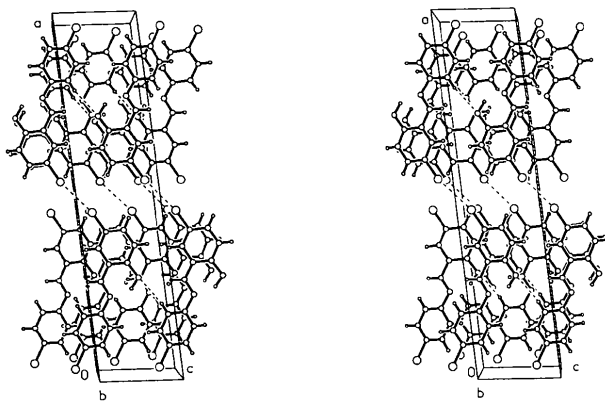


Fig. 5. The unit-cell packing of (3) viewed down the *b* axis showing the channels of Cl atoms and the stacking perpendicular to the *b* axis.

Experimental

The compounds were prepared by reacting salicylaldehyde with the appropriate aniline derivative. To an ethanolic solution of salicylaldehyde (1 M, 25 ml), a few drops of pH 5 HCl/NaOH solution were added to protonate the aldehyde. To this was added an ethanolic solution of the substituted aniline (1 M, 25 ml). The reaction mixture was refluxed with stirring for 1 h. The solutions were then cooled and the resulting precipitates were washed with water. Products were recrystallized from a CH₂Cl₂/*n*-hexane (1:10) solution.

Compound (1)

Crystal data

C₁₃H₁₀FNO
M_r = 215.22
 Monoclinic
*P*2₁/*c*
a = 12.820 (1) Å
b = 5.787 (1) Å
c = 14.817 (2) Å
 β = 107.93 (2)°
V = 1045.9 (2) Å³
Z = 4
D_x = 1.367 Mg m⁻³
D_m not measured

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: none
 2299 measured reflections
 1642 independent reflections
 1224 reflections with
 $I > 2\sigma(I)$
R_{int} = 0.020

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.037
wR(*F*²) = 0.096
S = 1.033
 1642 reflections
 150 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.1735P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Mo *K* α radiation

λ = 0.71073 Å
 Cell parameters from 23
 reflections
 θ = 5.44–12.43°
 μ = 0.099 mm⁻¹
T = 293 (2) K
 Block
 0.48 × 0.45 × 0.26 mm
 Yellow

θ_{\max} = 24°

h = -1 → 14
k = -1 → 6
l = -16 → 16
 3 standard reflections
 every 100 reflections
 intensity decay: <2%

(Δ/σ)_{max} < 0.001

$\Delta\rho_{\max}$ = 0.128 e Å⁻³
 $\Delta\rho_{\min}$ = -0.127 e Å⁻³

Extinction correction:

SHELXTL/PC (Sheldrick,
 1996)

Extinction coefficient:

0.014 (2)

Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Compound (2)

Crystal data

C₁₄H₁₀F₃NO₂
M_r = 281.23
 Monoclinic
*P*2₁/*c*
a = 5.647 (1) Å
b = 7.977 (2) Å
c = 29.197 (4) Å
 β = 90.63 (2)°
V = 1315.1 (4) Å³
Z = 4
D_x = 1.420 Mg m⁻³
D_m not measured

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: none
 3195 measured reflections

Mo *K* α radiation

λ = 0.71073 Å
 Cell parameters from 19
 reflections
 θ = 4.91–12.16°
 μ = 0.124 mm⁻¹
T = 293 (2) K
 Block
 0.38 × 0.38 × 0.22 mm
 Yellow

θ_{\max} = 24°

h = -1 → 6
k = -1 → 9
l = -33 → 33

2066 independent reflections 1128 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.030$	3 standard reflections every 100 reflections intensity decay: 1.5%	Monoclinic $P2_1/c$ $a = 12.413 (2) \text{ \AA}$ $b = 5.744 (2) \text{ \AA}$ $c = 15.597 (3) \text{ \AA}$ $\beta = 97.69 (2)^\circ$ $V = 1102.1 (5) \text{ \AA}^3$ $Z = 4$ $D_x = 1.460 \text{ Mg m}^{-3}$ D_m not measured	Cell parameters from 40 reflections $\theta = 5.28\text{--}12.00^\circ$ $\mu = 0.106 \text{ mm}^{-1}$ $T = 190 (2) \text{ K}$ Block $0.60 \times 0.40 \times 0.19 \text{ mm}$ Orange
Refinement Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.069$ $wR(F^2) = 0.189$ $S = 1.154$ 2066 reflections 186 parameters H atoms treated by a mixture of independent and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.1030P)^2 + 0.9747P]$ where $P = (F_o^2 + 2F_c^2)/3$	$(\Delta/\sigma)_{\text{max}} = 0.002$ $\Delta\rho_{\text{max}} = 0.436 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.229 \text{ e \AA}^{-3}$ Extinction correction: <i>SHELXTL/PC</i> (Sheldrick, 1996) Extinction coefficient: 0.070 (9) Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)	<i>Data collection</i> Siemens <i>P4</i> diffractometer ω scans Absorption correction: none 2393 measured reflections 1909 independent reflections 1418 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.040$	$\theta_{\text{max}} = 25^\circ$ $h = -14 \rightarrow 0$ $k = -6 \rightarrow 1$ $l = -18 \rightarrow 18$ 100 standard reflections every 3 reflections intensity decay: 3.2%
Compound (3) <i>Crystal data</i> $\text{C}_{13}\text{H}_9\text{Cl}_2\text{NO}$ $M_r = 266.11$ Monoclinic $P2_1/c$ $a = 27.419 (7) \text{ \AA}$ $b = 6.901 (2) \text{ \AA}$ $c = 6.137 (1) \text{ \AA}$ $\beta = 95.57 (2)^\circ$ $V = 1155.8 (5) \text{ \AA}^3$ $Z = 4$ $D_x = 1.529 \text{ Mg m}^{-3}$ D_m not measured	Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$ Cell parameters from 19 reflections $\theta = 5.14\text{--}12.33^\circ$ $\mu = 0.541 \text{ mm}^{-1}$ $T = 190 (2) \text{ K}$ Plate $0.64 \times 0.62 \times 0.29 \text{ mm}$ Yellow	Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.048$ $wR(F^2) = 0.124$ $S = 0.849$ 1909 reflections 167 parameters H atoms treated by a mixture of independent and constrained refinement	$w = 1/[\sigma^2(F_o^2) + (0.0768P)^2 + 1.6682P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.020$ $\Delta\rho_{\text{max}} = 0.171 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.178 \text{ e \AA}^{-3}$ Extinction correction: none Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
Compound (4) <i>Crystal data</i> $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3$ $M_r = 242.23$	Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$		
<i>Data collection</i> Siemens <i>P4</i> diffractometer ω scans Absorption correction: none 2375 measured reflections 1506 independent reflections 1352 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.027$	$\theta_{\text{max}} = 22.49^\circ$ $h = -29 \rightarrow 29$ $k = -7 \rightarrow 1$ $l = -1 \rightarrow 6$ 3 standard reflections every 100 reflections intensity decay: <1%		
Refinement Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.091$ $S = 1.129$ 1506 reflections 158 parameters H atoms treated by a mixture of independent and constrained refinement	$w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 0.7358P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.002$ $\Delta\rho_{\text{max}} = 0.215 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.223 \text{ e \AA}^{-3}$ Extinction correction: none Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)		

Table 1. Hydrogen-bonding geometry (\AA , $^\circ$) for compounds (1) to (4)

	O1—H1A	H1A...N1	O1—H1A...N1
Compound (1)	0.94 (3)	1.76 (3)	150 (2)
(2)	1.02 (6)	1.62 (7)	158 (5)
(3)	0.83 (3)	1.83 (3)	153 (3)
(4)	0.92 (3)	1.87 (3)	140 (3)

For all structures, the hydroxy-H1A atoms were located from difference Fourier maps and included as normal atoms in refinement cycles. All other H atoms were included in calculated positions (C—H = 0.96 \AA) with isotropic displacement parameters set to $1.2U_{\text{eq}}(\text{C})$.

For all compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1996); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1547). Services for accessing these data are described at the back of the journal.

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Recently, we have resorted to the related ability to staple the proton, and indirectly the bromide ion, in (–)-sparteinium bromide, (I), to resolve 1,2-dibromohexafluoropropane into single enantiomers (Farina *et al.*, 1999). This procedure relies on the self-assembly of the sparteinium bromide unit with one of the enantiomers of the perhalocarbon into a chiral cocrystal. Since the procedure is general, the crystal structure of (I) is reported herein to show how the interactions of additional species with the Br[–] ion influence the relation of the halide to the sparteinium ion.

Acta Cryst. (1999). **C55**, 1710–1711

(–)-Sparteinium bromide

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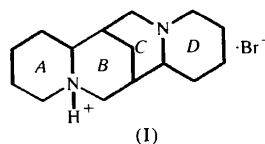
(Received 22 December 1998; accepted 16 June 1999)

Abstract

The title compound, (7*S*)-(7 α ,7 α ,14 α ,14 α)-1,3,4,7,7a,8,9,10,11,13,14,14a-dodecahydro-7,14-methano-2*H*,6*H*-dipyrido[1,2-*a*:1',2'-*e*][1,5]diazocin-5-ium bromide (C₁₅H₂₇N₂⁺·Br[–]), is an effective reagent for the resolution of chiral perhalocarbons. All four rings in the sparteinium ion adopt a chair conformation, allowing an intramolecular N—H···N hydrogen bond. Weak hydrogen-bond-like interactions between the cation and anion are apparent.

Comment

(–)-Sparteine is one of the best known members of the lupin alkaloids (Merck, 1989). It has been isolated from various *Lupinus* and *Cytisus* species and is widely distributed in the *Papilionaceae* (Hesse, 1981). From the pharmacological point of view, this alkaloid is endowed with oxytoxic activity, while from the chemical point of view it has been used effectively as a chiral catalyst and as a reagent in asymmetric synthesis (Hashihayata *et al.*, 1997; Nishimura *et al.*, 1997; Hoppe *et al.*, 1990). (–)-Sparteine has a semi-rigid structure; in the free base, ring *C* adopts a boat conformation but, upon chelation of a cation, inversion of configuration occurs on N16 and ring *C* adopts a chair conformation. In the resulting nest-like structure, the nitrogen lone pairs converge towards the centre of the molecular concavity, allowing an effective bidentate interaction with metal ions (Lopez *et al.*, 1998; Hoppe *et al.*, 1995; Motevalli *et al.*, 1993).



Consistent with the results and the literature data discussed by Kubicki *et al.* (1996), all four rings in the sparteinium ion of (I) adopt chair conformations, with the N16 configuration inverted with respect to that of the free base. In this conformation, the distance between N1 and N16 is 2.714 (8) Å, allowing an intramolecular hydrogen-bond interaction between N16 and the proton on N1 (Table 2). The structural and conformational features of the sparteinium ion in (I) are very similar to those found in the sparteinium hydrobromide–perhalocarbon cocrystal (Farina *et al.*, 1999). A significant difference is that the protonated nitrogen is N1 in the pure hydrobromide and N16 in the cocrystal. Shorter Br···N distances reasonably involve the protonated nitrogen, and accordingly the Br···N1 and the Br···N16 distances change from 3.552 (6) and 3.672 (6) in (I) to 3.622 (6) and 3.548 (6) Å in the cocrystal. Related minor differences involve the short quasi-hydrogen-bond interactions between cation H atoms and the bromide ion. Relevant parameters of these interactions for (I) are given in Table 2.

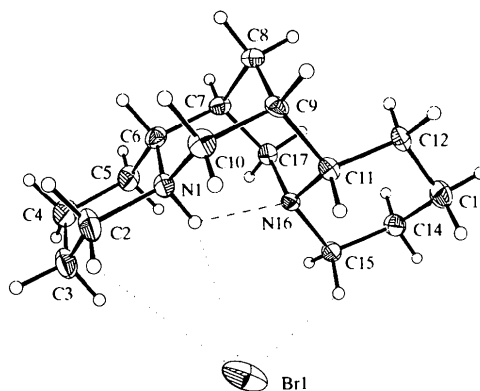


Fig. 1. A view of (I) showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 40% probability level, while H atoms are of an arbitrary size. Geometric parameters of the bromide ion interactions and of the hydrogen bond involving N16 are given in Table 2.