Table 6. *Hydrogen-bonding geometry (Å, °) for (3)*

D—H···A	D—H	H···A	D···A	D—H···A
N4A—H4A···Cl1	0.86	2.28	3.044 (2)	148
N12A—H12A···Cl1	0.86	2.41	3.195 (3)	152
N4B—H4B···Cl2	0.86	2.21	3.008 (3)	155
N12B—H12B···Cl2	0.86	2.57	3.368 (3)	155

The title structures were solved by direct methods and refined by full-matrix least squares on F^2. H atoms were included at calculated positions riding on their parent atoms. In compound (1), the 2-fluorophenyl ring has 180° rotational disorder with partial occupancy of the F atom. The sum of the occupation factors was constrained to 1. The occupation factor of the F2'A atom refined to 0.919 (6). In compound (2), difference Fourier maps showed a 180° rotational disorder of the thienyl ring. The ring was modelled by two superimposed thiophene rings and refined as two parts with same-distance restraints. The occupation factor of part A refined to 0.573 (7). Compound (3) contains two benzodiazepine molecules and one isobutyl methyl ketone molecule in the asymmetric unit. Although the ratio of the number of reflections to the number of parameters [8.99, 8.88 and 7.87 for compounds (1), (2) and (3), respectively] is lower than 8 for compound (3), the reliability of the corresponding bonds and angles in the three structures is of the same order of magnitude.

For all compounds, data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PARST* (Nardelli, 1983).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1340). Services for accessing these data are described at the back of the journal.

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N-(2-Bromo-4-methylphenyl)naphthaldimine

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Abstract

Molecules of the title compound [1-(2-bromo-4-methyl-phenyliminomethyl)-2-naphthol, $C_{18}H_{14}BrNO$] are not exactly planar. Each contains a strong intramolecular N···H—O hydrogen bond between the amino and hydroxyl groups [2.553 (4) Å].

Comment

Although many structures of transition metal complexes with Schiff bases have been determined, a relatively small number of free Schiff bases have been structurally characterized (Calligaris & Randaccio, 1987). In the course of a systematic structural investigation of Schiff bases (Elerman *et al.*, 1991, 1992, 1994, 1995, 1997, 1998; Elmali *et al.*, 1995, 1998; Elmali & Elerman, 1997, 1998; Kevran *et al.*, 1996), the structure of the title compound, (I), was determined.

(I)
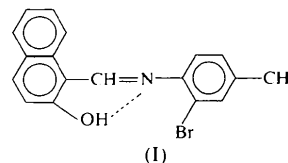
Schiff bases are of interest because they have long been known to show photochromism and thermochromism in the solid state which may involve reversible proton transfer from the amino N atom to the hydroxyl O atom (Cohen *et al.*, 1964; Moustakali *et al.*, 1978; Hadjoudis *et al.*, 1987).

The title molecule is not exactly planar; moieties A [Br1, N1, C1–C7; planar with a maximum deviation of 0.016 (3) Å for the C4 atom] and B [O1, C8–C18; planar with a maximum deviation of 0.073 (3) Å for the C8 atom] are inclined at an angle of 7.2 (1)°, reflecting mainly the twist about C7—N1 [C6—C7—N1—C8 −7.5 (6)°].

Two types of intramolecular hydrogen bonds, either N—H···O or N···H—O, can exist in Schiff bases (Garnovskii *et al.*, 1993). The Schiff bases derived from salicylaldehyde always form N···H—O-type hydrogen

bonds regardless of the substituent (alkyl or aryl) on the N atom (Gavranić *et al.*, 1996). In the aldimine compounds formed from 2-hydroxy-1-naphthaldehyde, both types of hydrogen bonds were found (Kaitner & Pavlović, 1996; Elerman *et al.*, 1997). In (I), a strong intramolecular hydrogen bond links the N1 and O1 atoms [2.553 (4) Å]. The H1O atom was found in a difference electron-density map at the end of the refinement process as a small positive electron density. The N1···H1O and O1—H1O bond distances are 1.71 and 0.97 Å, respectively, and the N1···H—O1 angle is 143.2°. The sum of the van der Waals radii of N and O (3.07 Å) is significantly longer than the intramolecular N···O hydrogen-bond length (Bondi, 1964).
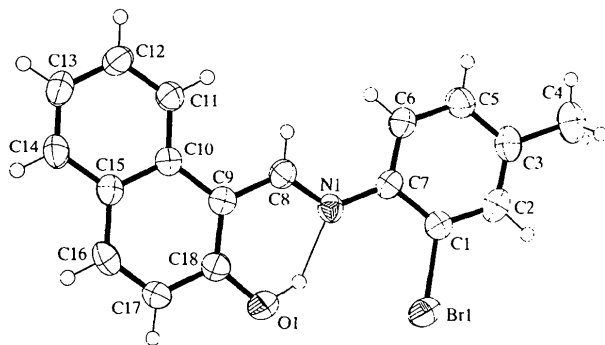

Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids (*ORTEP*II; Johnson, 1976).

Experimental

The title compound was obtained from the reaction of 2-hydroxynaphthalene-1-carbaldehyde (0.01 mol, 1.722 g) with a solution of 2-bromo-4-methylaniline (0.01 mol, 1.861 g) in 40 ml of ethanol. The precipitate which separated from the solution was recrystallized for 1–2 d from 1.7 g of Schiff base in 70 ml of acetonitrile solution.

Crystal data

$C_{18}H_{14}BrNO$
$M_r = 340.21$
Monoclinic
$P2_1$
$a = 6.1373 (6)$ Å
$b = 8.979 (2)$ Å
$c = 13.3554 (10)$ Å
$\beta = 96.880 (5)°$
$V = 730.69 (19)$ Å^3
$Z = 2$
$D_x = 1.546$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 3.40–8.12°$
$\mu = 2.810$ mm^{-1}
$T = 293 (2)$ K
Prism
$0.32 \times 0.20 \times 0.14$ mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction:
  ψ scan (*SDP-Plus*; Frenz, 1985)
  $T_{min} = 0.535$, $T_{max} = 0.675$
3681 measured reflections
3680 independent reflections

2800 reflections with $I > 2\sigma(I)$
$R_{int} = 0.001$
$\theta_{max} = 28.97°$
$h = 0 \rightarrow 8$
$k = -11 \rightarrow 12$
$l = -18 \rightarrow 17$
3 standard reflections
  frequency: 120 min
  intensity decay: 0.09%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.094$
$S = 1.254$
3680 reflections
190 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 0.3886P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.016$

$\Delta\rho_{max} = 0.260$ e Å^{-3}
$\Delta\rho_{min} = -0.330$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for Crystallography (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = $-0.008 (12)$

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

Br1—C1	1.897 (4)	N1—C8	1.291 (4)
C7—N1	1.403 (5)	C18—O1	1.321 (5)
C2—C1—Br1	118.6 (3)	C8—N1—C7	124.1 (3)
C7—C1—Br1	118.8 (3)	N1—C8—C9	121.9 (3)
C1—C7—N1	119.3 (3)	O1—C18—C9	122.7 (4)
C6—C7—N1	124.3 (3)	O1—C18—C17	116.9 (4)

The title structure was solved by direct phase determination. The parameters of the complete structure were refined by full-matrix anisotropic least squares. The phenyl rings were refined without any constraints. Distances and angles in the rings show no significant differences from those of an ideal benzene ring. All H-atom positions (except for the H1O atom) were calculated using a riding model and were considered with fixed isotropic U values in all refinements. The H1O atom was found in the difference electron-density maps calculated at the end of the refinement process as a small positive electron density and was not refined.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *MolEN* (Fair, 1990). Data reduction: *MolEN*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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3α-Bikhaconine Acetone Solvate

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Abstract

The crystal structure of 3α-bikhaconine acetone solvate [1α,6α,16β-trimethoxy-4β-(methoxymethyl)aconitane-

3α,8β,13β,14α-tetrol acetone solvate, $C_{25}H_{41}NO_8$.C_3H_6O], a C_{19} norditerpenoid alkaloid which has been partially synthesized from indaconitine, contains discrete molecules separated by normal van der Waals distances. The molecular dimensions are normal; the mean bond distances are C_{sp^3}—N 1.471 (9), C_{sp^3}—C_{sp^3} 1.54 (2) and C_{sp^3}—O 1.425 (14) Å. The fused-ring system contains two chair, one half-chair, two envelope and one boat conformation. There are both inter- and intramolecular hydrogen bonds, with O···O separations in the range 2.655 (3)–3.048 (3) Å and H···O interactions in the range 1.92–2.38 Å. There are no interactions between the alkaloid and the solvate molecules.

Comment

Continuing our crystallographic studies of C_{19} norditerpenoid alkaloids (Parvez, Gul, Anwar *et al.*, 1998; Parvez, Gul & Anwar, 1998*a,b*), we now report the crystal structure of 3α-bikhaconine, (1), as its acetone solvate. The alkaloid was originally isolated from the roots of *Aconitum chasmanthum* Stapf ex Holmes of Pakistani origin, but its quantity was insufficient to grow crystals for X-ray diffraction studies. It was subsequently synthesized from indaconitine, which was isolated from the same plant.
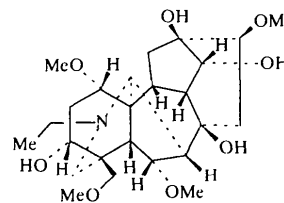
(1)

The crystal structure contains independent molecules of 3α-bikhaconine (Fig. 1) and acetone solvate separated by normal van der Waals distances. The absolute structure could not be established in this analysis and the absolute structure reported in this article is the same as that known for chasmanine 14α-benzoate hydrochloride (De Camp & Pelletier, 1977). The molecular dimensions in (1) are normal and lie within expected values for the corresponding bond distances and angles, with mean bond distances C_{sp^3}—N 1.471 (9), C_{sp^3}—C_{sp^3} 1.54 (2) and C_{sp^3}—O 1.425 (14) Å.

The six-membered rings *A* (C1–C5, C11) and *E* (C4, C5, C11, C17, N1, C19) adopt chair conformations. Ring *A* is slightly flattened at C1 due to the methoxy substituent attached to C1, as observed in the structures of a chasmanine intermediate (Przybylska & Ahmed, 1980), aconitine (Codding, 1982), chasmaconitine methanol solvate (Parvez, Gul, Anwar *et al.*, 1998) and chasmanthinine (Parvez, Gul & Anwar, 1998*a*). Ring *E* is also slightly flattened at C19 due to the presence of an ethyl-substituted N atom in the ring. The six-membered ring *D* (C8, C9, C13–C16) has a half-