NMR ($CDCl_3$, 300 MHz, TMS) δ = 7.05 (*s*, 4H, H2,3,5,6), 7.29 (*m*, 4H, H4′,5′), 8.37 (*dd*, 2H, *J* = 1.8, 3.9 Hz, H6′), 8.41 (*t*, 2H, *J* = 1.5 Hz, H2′). Recrystallization from ethyl acetate gave a mass of crystals from which a suitable crystal was cut.

Crystal data

$C_{16}H_{12}N_2O_2$
M_r = 264.28
Monoclinic
$P2_1/c$
a = 6.9174 (4) Å
b = 7.4267 (4) Å
c = 12.0693 (7) Å
β = 98.206 (3)°
V = 613.69 (6) Å^3
Z = 2
D_x = 1.430 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 2080 reflections
θ = 3.0–26.9°
μ = 0.096 mm^{-1}
T = 158 (2) K
Block
0.48 × 0.44 × 0.32 mm
Beige

Data collection

Siemens SMART CCD diffractometer
Exposures over 0.3° φ or ω rotation scans
Absorption correction: none
1988 measured reflections
903 independent reflections
823 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 25.85°
$h = -3 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -9 \rightarrow 14$
No standard reflections
Intensity decay: 10%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.105
S = 1.09
903 reflections
91 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.1532P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.175 e Å^{-3}
$\Delta\rho_{min}$ = −0.178 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—C2	1.379 (2)	N1′—C2′	1.339 (2)
C1—C3^i	1.383 (2)	C2′—C3′	1.381 (2)
C1—O1	1.399 (2)	C3′—C4′	1.384 (2)
C2—C3	1.383 (2)	C4′—C5′	1.381 (2)
O1—C3′	1.380 (2)	C5′—C6′	1.382 (2)
N1′—C6′	1.334 (2)		
C2—C1—C3^i	120.05 (13)	N1′—C2′—C3′	122.94 (13)
C2—C1—O1	115.98 (12)	O1—C3′—C2′	117.49 (13)
C3^i—C1—O1	123.94 (13)	O1—C3′—C4′	122.73 (12)
C1—C2—C3	120.21 (13)	C2′—C3′—C4′	119.69 (13)
C1^i—C3—C2	119.75 (13)	C5′—C4′—C3′	117.60 (13)
C3′—O1—C1	118.18 (10)	C4′—C5′—C6′	119.09 (13)
C6′—N1′—C2′	116.90 (12)	N1′—C6′—C5′	123.73 (14)

Symmetry code: (i) $2-x, -y, 1-z$.

Crystal decay was monitored by measurement of duplicate reflections.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXL*93. Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1207). Services for accessing these data are described at the back of the journal.

References

Bacon, R. G. R. & Stewart, O. J. (1965). *J. Chem. Soc.* pp. 4953–4961.
Clayden, N. J., Williams, D. & O'Mahoney, C. A. (1990). *J. Chem. Soc. Perkin Trans.* 2, pp. 729–733.
Drendel, W. B. & Sundaralingam, M. (1985). *Acta Cryst.* C**41**, 950–953.
Fujita, M. & Ogura, K. (1996). *Bull. Chem. Soc. Jpn*, **69**, 1471–1482.
Hartshorn, C. M. & Steel, P. J. (1996). *Inorg. Chem.* **35**, 6902–6903.
Hunter, C. A. & Sanders, J. K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.
Katritzky, A. R., Ghiviriga, I., Steel, P. J. & Oniciu, D. C. (1996). *J. Chem. Soc. Perkin Trans.* 2, pp. 443–447.
Pavia, M. R., Taylor, C. P., Hershenson, F. M., Lobbestael, S. J. & Butler, D. E. (1988). *J. Med. Chem.* **31**, 841–847.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1995). *SMART* and *SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). C**54**, 1133–1137

(−)-(2*S*)-Tifluadom Hydrochloride and Two of its (−)-(2*S*)-2-(Acylaminomethyl)-benzodiazepine Hydrochloride Analogues

OSWALD M. PEETERS, RITA L. MEURISSE, NORBERT M. BLATON AND CAMIEL J. DE RANTER

Laboratorium voor Analytische Chemie en Medicinale Fysicochemie, Faculteit Farmaceutische Wetenschappen, Katholieke Universiteit Leuven, Van Evenstraat 4, B-3000 Leuven, Belgium. E-mail: maurice.peeters@farm.kuleuven.ac.be

(*Received 25 November 1997; accepted 25 February 1998*)

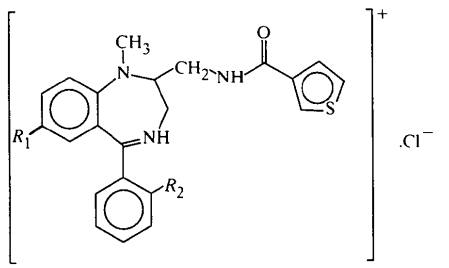
Abstract

The structures of three (−)-(2*S*)-(acylaminomethyl)-benzodiazepine hydrochlorides, namely, 5-(2-fluorophenyl)-1-methyl-2-(3-thenoylaminomethyl)-2,3-dihydro-1*H*-1,4-benzodiazepin-4-ium chloride [$C_{22}H_{21}FN_3OS^+.Cl^-$, (1), tifluadom], 1,7-dimethyl-5-phenyl-2-(3-thenoylaminomethyl)-2,3-dihydro-1*H*-1,4-benzodiazepin-4-ium chloride [$C_{23}H_{24}N_3OS^+.Cl^-$, (2)] and 5-(4-fluorophenyl)-1,8-dimethyl-2-(*p*-toluoylaminomethyl)-2,3-

dihydro-1*H*-1,4-benzodiazepin-4-ium chloride hemi(isobutyl methyl ketone) solvate [$C_{26}H_{27}FN_3O^+.Cl^-.0.5C_6H_{12}O$, (3)] are reported. The conformations of the molecules are very similar. The seven-membered ring has a conformation halfway between a distorted boat and a distorted sofa, with the 2-substituent in a flagpole orientation and the acylaminomethyl moiety in an extended conformation.

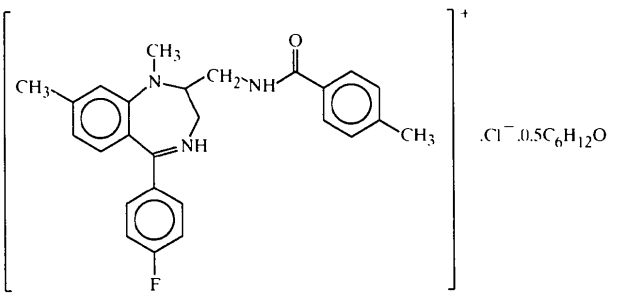
Comment

As part of a structure–affinity study on κ-opioids related to tifluadom, the crystal structures of a number of 2-(acylaminomethyl)benzodiazepine derivatives have been determined (Peeters *et al.*, 1997, and references therein). The crystals used in these structure analyses were obtained from the racemic compounds. In order to obtain reliable pharmacological data the racemic mixtures were separated into their enantiomers by high-performance liquid chromatography (Meurisse & De Ranter, 1994). The separated enantiomers were then crystallized as hydrochloric salts and their optical activity determined. The pharmacological data revealed that in all cases the (−)-enantiomer of the hydrochloric salts has the highest κ-opioid affinity (Meurisse, 1997). Petcher *et al.* (1985) determined the crystal structure and absolute configuration of (+)-tifluadom *p*-toluenesulfonate. The absolute configuration is 2*S*, using standard chemical numbering. They reported also that the analgesic activity resides principally in the (+)-enantiomer. To clear up the contradiction, we determined the crystal structure and absolute configuration of the (−)-hydrochloric salts of tifluadom, (1), KC5050, (2), and KC6132, (3). For these three structures, the Flack parameter (Flack, 1983) indicates the 2*S* configuration. Our results confirm the observation of Petcher *et al.* (1985) that the principal κ-opioid activity resides in the 2*S* configuration. The (+)-optical rotation sign for the (2*S*)-tifluadom *p*-toluenesulfonate salt reported by Petcher *et al.* (1985) belongs presumably to the tifluadom base, as the (−)-optical rotation sign of the (2*S*)-hydrochloric salts becomes + when one drop of 30% $NaOCH_3$ in MeOH is added.



(1) R_1 = H ; R_2 = F
(2) R_1 = CH_3; R_2 = H

The crystal structure of tifluadom hydrochloride has been determined previously (Petcher *et al.*, 1985). Starting from the racemate, the compound crystallized in the non-centrosymmetric space group $P2_12_12_1$ so that individual crystals contain exclusively one or the other enantiomer. The cell parameters and geometric parameters agree within experimental error with those of compound (1). The structure of the racemate of compound (2) has been described by Blaton *et al.* (1996). An r.m.s. fit (Hypercube, 1993) of the corresponding non-H atoms (except for those of the disordered thienyl group) of the molecular structure in the racemate and in compound (2) gives an r.m.s. value of 0.166 Å, indicating an almost identical conformation.



(3)

The geometric parameters of the three structures show only small deviations from each other and from those of the other structures of the series. The puckering parameters and asymmetry parameters for the seven-membered ring indicate a global conformation halfway between a distorted boat and a distorted sofa, with a pseudo-mirror plane through C3 and the middle of the opposite bond. The axially positioned 2-acylaminomethyl substituent always adopts an extended conformation, which is stabilized by two hydrogen bonds to the Cl^- anion, one from the protonated basic N atom of the heptadiene ring and another from the amidic N atom.

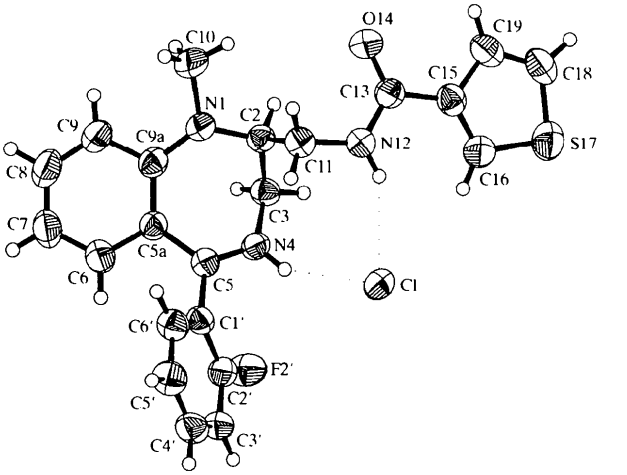


Fig. 1. Perspective view of compound (1) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

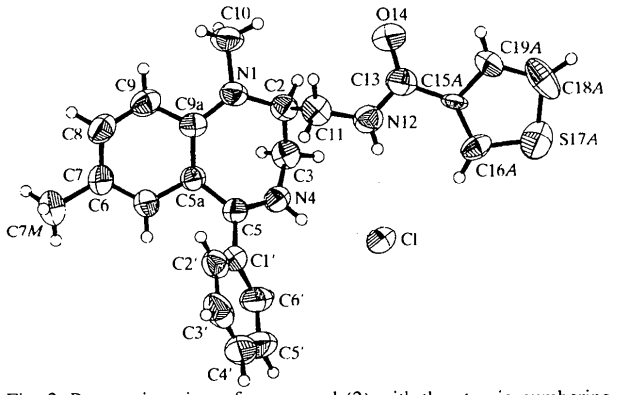


Fig. 2. Perspective view of compound (2) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

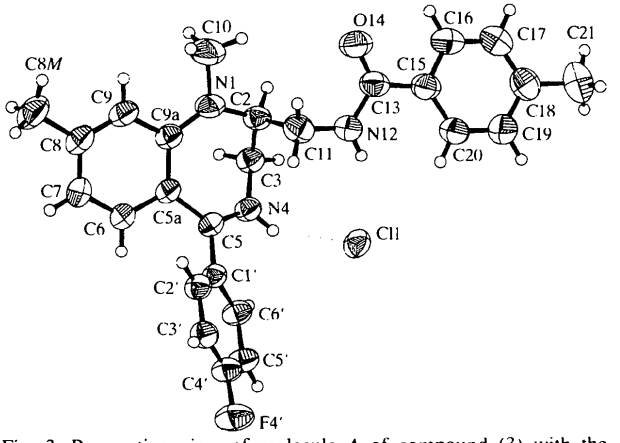


Fig. 3. Perspective view of molecule *A* of compound (3) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The racemic mixtures of the title compounds were originally gifts from Kali-Chemie Pharma GmbH, Hannover, Germany. The bases were resynthesized according to a method described by Meurisse (1997) and separated into their enantiomers by chiral high-performance liquid chromatography (Meurisse & De Ranter, 1994). After evaporation to dryness, the separate enantiomers were treated with toluene and again evaporated to dryness. The residues were dissolved in isobutyl methyl ketone, heated slowly and a solution of HCl (6 *N*) in 2-propanol solution was added until an acidic pH was achieved. After hydrochloric salt formation, the solution was evaporated to dryness, redissolved in acetone and allowed to crystallize by slow evaporation at room temperature. The specific optical rotation values $[\alpha]_D^{20}$ (0.1% in MeOH) were −591.5, −310.8 and −305.4° for compounds (1), (2) and (3), respectively. The crystals used in the diffraction experiments were obtained from methanol/ethyl acetate solutions.

Compound (1)

Crystal data

$C_{22}H_{21}FN_3OS^+.Cl^-$
M_r = 429.93
Orthorhombic
$P2_12_12_1$
a = 6.4494 (6) Å
b = 15.000 (1) Å
c = 21.334 (1) Å
V = 2064.0 (3) Å^3
Z = 4
D_x = 1.384 Mg m^{-3}
D_m = 1.382 Mg m^{-3}
D_m measured by flotation in *n*-heptane/CCl_4
Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 39 reflections
θ = 11.02–27.93°
μ = 2.810 mm^{-1}
T = 293 K
Prism
0.44 × 0.34 × 0.10 mm
Red–orange

Data collection

Siemens *P*4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*XEMP*; Siemens, 1989)
T_{min} = 0.330, T_{max} = 0.755
2691 measured reflections
1995 independent reflections
1925 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.069
θ_{max} = 67.96°
h = −1 → 7
k = −1 → 18
l = −1 → 25
3 standard reflections
every 100 reflections
intensity decay: 6.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.123
S = 1.069
2463 reflections
274 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0889P)^2 + 0.2960P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0050 (7)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute structure: Flack (1983)
Flack parameter = 0.02 (2)

Table 1. *Selected torsion angles (°) for (1)*

C2—N1—C9a—C5a	29.8 (5)	C3—N4—C5—C5a	−3.0 (4)
C10—N1—C9a—C9	2.1 (4)	N4—C5—C1'—C2'	−49.5 (4)
C9a—N1—C2—C3	10.1 (4)	N4—C5—C5a—C9a	−34.8 (4)
N1—C2—C11—N12	−169.3 (2)	C5—C5a—C9a—N1	−0.2 (5)
N1—C2—C3—N4	−72.5 (3)	C2—C11—N12—C13	80.0 (3)
C11—C2—C3—N4	53.3 (3)	C11—N12—C13—C15	−175.5 (3)
C2—C3—N4—C5	71.7 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···Cl	0.86	2.24	3.022 (3)	152
N12—H12···Cl	0.86	2.50	3.268 (3)	150

Compound (2)

Crystal data

$C_{23}H_{24}N_3OS^+.Cl^-$
M_r = 425.96
Cu $K\alpha$ radiation
λ = 1.54184 Å

Orthorhombic
$P2_12_12_1$
a = 6.3344 (2) Å
b = 13.5131 (7) Å
c = 25.693 (2) Å
V = 2199.2 (2) Å^3
Z = 4
D_x = 1.287 Mg m^{-3}
D_m = 1.281 Mg m^{-3}
D_m measured by flotation in *n*-heptane/CCl_4

Cell parameters from 39 reflections
θ = 10.92–27.23°
μ = 2.570 mm^{-1}
T = 293 K
Plate
0.46 × 0.22 × 0.04 mm
Red–orange

Data collection

Siemens *P*4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scan (*XEMP*; Siemens, 1989)
T_{min} = 0.555, T_{max} = 0.902
3007 measured reflections
2204 independent reflections

1864 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.051
θ_{max} = 69.06°
$h = -1 \rightarrow 7$
$k = -1 \rightarrow 16$
$l = -1 \rightarrow 31$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.137
S = 1.042
2761 reflections
311 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0789P)^2 + 0.7366P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Extinction correction:
*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient:
0.0059 (6)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute structure: Flack (1983)
Flack parameter = −0.01 (3)

a = 11.9932 (3) Å
b = 19.667 (1) Å
c = 12.9428 (7) Å
β = 117.471 (4)°
V = 2708.6 (2) Å^3
Z = 4
D_x = 1.231 Mg m^{-3}
D_m = 1.230 Mg m^{-3}
D_m measured by flotation in *n*-heptane/CCl_4

μ = 1.530 mm^{-1}
T = 293 K
Prism
0.58 × 0.38 × 0.15 mm
Pale orange

Data collection

Siemens *P*4 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction:
ψ scan (*XEMP*; Siemens, 1989)
T_{min} = 0.572, T_{max} = 0.795
5940 measured reflections
4827 independent reflections

4691 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.020
θ_{max} = 67.33°
$h = -1 \rightarrow 13$
$k = -23 \rightarrow 1$
$l = -15 \rightarrow 14$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.105
S = 1.084
5115 reflections
650 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.3714P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Extinction correction:
*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient:
0.0044 (3)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (1)

Table 3. *Selected torsion angles (°) for (2)*

C2—N1—C9a—C5a	25.6 (5)	C3—N4—C5—C5a	−3.2 (5)
C10—N1—C9a—C9	3.9 (5)	N4—C5—C1′—C6′	−42.8 (5)
C9a—N1—C2—C3	20.8 (5)	N4—C5—C5a—C9a	−25.5 (5)
N1—C2—C11—N12	−174.4 (3)	C5—C5a—C9a—N1	−8.8 (6)
N1—C2—C3—N4	−76.0 (4)	C2—C11—N12—C13	94.8 (4)
C11—C2—C3—N4	50.6 (4)	C11—N12—C13—C15*A*	173.9 (7)
C2—C3—N4—C5	66.9 (4)	C11—N12—C13—C15*B*	173 (1)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4···Cl	0.86	2.24	3.047 (3)	155
N12—H12···Cl	0.86	2.50	3.336 (3)	164

Compound (3)

Crystal data

$C_{26}H_{27}FN_3O^+.Cl^-.0.5C_6H_{12}O$
M_r = 502.04
Monoclinic
$P2_1$

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 38 reflections
θ = 10.60–27.96°

Table 5. *Selected torsion angles (°) for (3)*

C2*A*—N1*A*—C9a*A*—C5a*A*	18.5 (5)
C10*A*—N1*A*—C9a*A*—C9a	6.3 (5)
C9a*A*—N1*A*—C2*A*—C3*A*	23.1 (4)
N1*A*—C2*A*—C11*A*—N12*A*	−165.0 (3)
N1*A*—C2*A*—C3*A*—N4*A*	−77.2 (3)
C11*A*—C2*A*—C3*A*—N4*A*	48.0 (4)
C2*A*—C3*A*—N4*A*—C5a	68.0 (4)
C3*A*—N4*A*—C5a—C5a*A*	−1.9 (5)
N4*A*—C5a—C1′*A*—C6′*A*	−33.7 (4)
N4*A*—C5a—C5a*A*—C9a*A*	−32.4 (5)
C5a—C5a*A*—C9a*A*—N1*A*	1.1 (5)
C2*A*—C11*A*—N12*A*—C13*A*	88.9 (4)
C11*A*—N12*A*—C13*A*—C15*A*	178.7 (3)
C2*B*—N1*B*—C9a*B*—C5a*B*	13.6 (6)
C10*B*—N1*B*—C9a*B*—C9*B*	2.6 (5)
C9a*B*—N1*B*—C2*B*—C3*B*	26.8 (5)
N1*B*—C2*B*—C11*B*—N12*B*	−170.7 (3)
N1*B*—C2*B*—C3*B*—N4*B*	−77.2 (4)
C11*B*—C2*B*—C3*B*—N4*B*	48.8 (4)
C2*B*—C3*B*—N4*B*—C5*B*	67.5 (4)
C3*B*—N4*B*—C5*B*—C5a*B*	−5.0 (5)
N4*B*—C5*B*—C1′*B*—C2′*B*	−36.1 (4)
N4*B*—C5*B*—C5a*B*—C9a*B*	−27.9 (5)
C5*B*—C5a*B*—C9a*B*—N1*B*	1.1 (6)
C2*B*—C11*B*—N12*B*—C13*B*	86.5 (4)
C11*B*—N12*B*—C13*B*—C15*B*	177.6 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4*A*—H4*A*···Cl1	0.86	2.28	3.044 (2)	148
N12*A*—H12*A*···Cl1	0.86	2.41	3.195 (3)	152
N4*B*—H4*B*···Cl2	0.86	2.21	3.008 (3)	155
N12*B*—H12*B*···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.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Bergerhoff, G. (1996). *DIAMOND. Visual Crystal Information System.* Bonn, Germany.

Blaton, N. M., Peeters, O. M. & De Ranter, C. J. (1996). *Acta Cryst.* C**52**, 2793–2795.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hypercube (1993). *CHEMPLUS: Extensions for Hyperchem.* Hypercube Inc., Waterloo, Ontario, Canada.

Meurisse, R. L. (1997). PhD thesis, Katholieke Universiteit Leuven, Belgium.

Meurisse, R. L. & De Ranter, C. J. (1994). *Chromatographia*, **38**, 629–632.

Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.

Peeters, O. M., Blaton, N. M. & De Ranter, C. J. (1997). *Acta Cryst.* C**53**, 95–97.

Petcher, T. J., Widmer, A., Maetzel, U. & Zeugner, H. (1985). *Acta Cryst.* C**41**, 909–912.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1996). *XSCANS. X-ray Single Crystal Analysis Software.* Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1989). *XEMP. Empirical Absorption Correction Program.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). C**54**, 1137–1139

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

AYHAN ELMALI,[a] YALÇIN ELERMAN[a] AND ENGIN KENDİ[b]

[a]*Department of Physics Engineering, Faculty of Sciences, University of Ankara, 06100 Besevler, Ankara, Turkey, and* [b]*Department of Physics Engineering, Hacettepe University, 06532 Beytepe, Ankara, Turkey. E-mail: elmali@science.ankara.edu.tr*

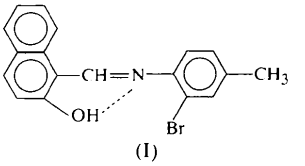
(Received 12 January 1998; accepted 16 February 1998)

Abstract

Molecules of the title compound [1-(2-bromo-4-methylphenyliminomethyl)-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