formed were removed by repeated washing with CCl_4. The yield of the complex was 0.180 g. Analysis found: C 21.87, H 3.68, N 3.60, Se 20.6, I 32.5%; calculated: C 21.87, H 3.69, N 3.66, Se 20.66, I 33.21%.

Crystal data

[SeI($C_7H_{14}NS_2$)]	Mo $K\alpha$ radiation
M_r = 382.17	λ = 0.71069 Å
Orthorhombic	Cell parameters from 36 reflections
$P2_12_12_1$	θ = 8–25°
a = 6.905 (3) Å	μ = 5.609 mm^{-1}
b = 11.050 (6) Å	T = 293 (2) K
c = 16.835 (2) Å	Needle
V = 1284.5 (9) Å^3	0.42 × 0.12 × 0.12 mm
Z = 4	Red–brown
D_x = 1.976 Mg m^{-3}	
D_m not measured	

Data collection

Siemens $P4$ diffractometer	1037 reflections with $I > 2\sigma(I)$
θ–2θ scans	θ_{max} = 24.97°
Absorption correction: ψ scan (*XSCANS*; Siemens, 1994)	h = 0 → 8
T_{min} = 0.374, T_{max} = 0.510	k = 0 → 13
1279 measured reflections	l = 0 → 20
1279 independent reflections	3 standard reflections every 97 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ < 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.035	$\Delta\rho_{max}$ = 0.392 e Å^{-3}
$wR(F^2)$ = 0.094	$\Delta\rho_{min}$ = −0.513 e Å^{-3}
S = 1.092	Extinction correction: none
1279 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
109 parameters	
H atoms were fixed geometrically and refined using a riding model	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 1.4891P]$ where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter = 0.00 (4)

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

I—Se	3.124 (2)	Se—I^i	3.232 (1)
Se—S2	2.277 (3)	S1—C1	1.729 (11)
Se—S1	2.298 (3)	S2—C1	1.725 (11)
S2—Se—S1	76.84 (11)	C1—S1—Se	85.8 (4)
S2—Se—I	77.66 (8)	C1—S2—Se	86.5 (4)
S1—Se—I^i	75.23 (8)	S2—C1—S1	110.8 (6)
I—Se—I^i	130.11 (4)		

Symmetry code: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$.

The disorder in atoms C3 and C4 could not be resolved satisfactorily by assigning partial sites.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). 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.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1008). Services for accessing these data are described at the back of the journal.

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(*S*)-8-Chloro-5-methyl-6-(3-methylbut-2-enyl)-2-thioxo-1*H*-4,5,6,7-tetrahydroimidazo[4,5,1-*jk*][1,4]benzodiazepinium bromide methanol solvate†

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Abstract

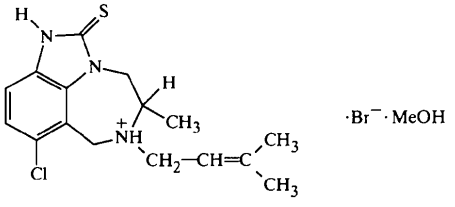
The crystal structure of the title compound, $C_{16}H_{21}ClN_3S^+ \cdot Br^- \cdot CH_3OH$, the hydrobromide salt of (*S*)-8-Cl-TIBO (tivirapine), reveals a distorted boat–sofa conformation for the diazepine ring, with the methyl group and the 3-methylbut-2-enyl side chain in equatorial and axial positions, respectively. The protonated N atom has

† Internal code of the Janssen Research Foundation: R110885.

the *S* configuration. A conformational analysis of (*S*)-8-Cl-TIBO shows the conformational flexibility of this HIV-1 inhibitor.

Comment

The title compound, (I), is the hydrobromide salt of R86183 (8-Cl-TIBO, tivirapine), which was the most potent of a very large series of compounds referred to under the acronym TIBO. Compounds of this series were the first non-nucleoside compounds reported to inhibit the human immunodeficiency virus type 1 (HIV-1) (Pauwels *et al.*, 1990). Studies show that the compounds are completely specific for HIV-1 and have no inhibitory effect on HIV-2. The mechanism of action has been determined to be inhibition of reverse transcriptase (RT), but the inhibition is non-competitive as binding takes place at an allosteric site proximal to the active site of the enzyme. Das *et al.* (1996) reported some TIBO analogues as a cocrystal within the binding pocket of RT. Compared with the crystal structure of 9-Cl-TIBO (Liaw *et al.*, 1991), most of the bond lengths do not show outstanding features. The bonds of the N6 atom are lengthened due to protonation. The bond angles of the benzimidazole and methylbutenyl moieties have comparable values, although the position of the Cl substituent shows its influence on the internal angles of the phenyl ring. The most striking differences are in the internal angles of the seven-membered ring and are a consequence of the different ring conformations.



(I)

In the title compound, the puckering parameters [for sequence N3, C4–C10b, q_2 = 0.829 (5), q_3 = 0.313 (5), Q_T = 0.886 (5) Å, φ_2 = 112.5 (3), φ_3 = −16.3 (8), θ_2 = 69.3 (3)°] and asymmetry parameter [Δ_S(C10b) = 0.076 (1)] indicate a boat–sofa conformation with a pseudo-mirror plane through the C10b atom and the centre of the opposite bond. Both the C5 and the N6 atoms have an *S* configuration and above the benzimidazole plane (an atom is defined as being above the plane when the numbering of the diazepine ring is clockwise when viewed down from the atom). The methyl and methylbutenyl substituents are in equatorial and axial positions, respectively. The stern of the boat–sofa is distorted, with a displacement of the C5 atom in the direction of the benzimidazole ring so as to overcome the energy associated with an eclipsed conformation.

In the crystal structure of (*S*)-9-Cl-TIBO, there are two independent molecules (designated *A* and *B*) in the asymmetric unit having rather different conformations. In both conformations, the N6 atom has the *R* configuration, which is opposite to that in the title compound. Molecule *A* has its seven-membered diazepine ring in a twist-sofa conformation, with the methyl group in an equatorial position and the methylbutenyl moiety in an axial position. Molecule *B* adopts a distorted boat–sofa conformation, with both substituents in equatorial positions. The distortion is opposite to that in the title compound, with the N6 atom displaced in the direction of the benzimidazole ring.

In a crystal structure of HIV-1 RT complexed with (*S*)-9-Cl-TIBO (Ren *et al.*, 1995), a fourth conformation was found, with the diazepine ring in a twist-sofa conformation and both substituents in axial positions. Since three atoms of the seven-membered ring are part of the planar benzimidazole system, the conformational flexibility should be mainly determined by the remaining four saturated atoms. A molecular-mechanics conformational search with the *MM*$^+$ force field (Hypercube, 1993, 1994) of the 5,6-dimethyl analogue of (*S*)-8-Cl-TIBO, with random variation of the internal torsion angles of the diazepine ring and discarding the C5 *R* configurations, revealed 11 different conformations, within 3.8 kcal mol^{-1} (1 cal = 4.184 J) above the global minimum. All four possible twist-sofa and seven of the eight possible distorted boat–sofa forms [N6: *R* or *S*; C5: above (*a*) or below (*b*) the benzimidazole plane; stern distortion torsion angle: positive (+) or negative (−)] were present. The eighth boat–sofa conformation (*S*, *b*,

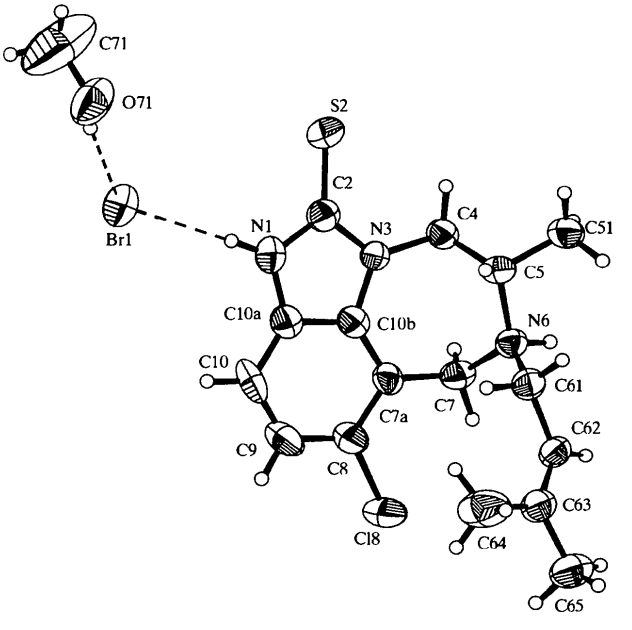


Fig. 1. Perspective view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

+) always refined to the lowest energy boat–sofa conformation (*S*, *b*, −). An identical conformational search of (*S*)-8-Cl-TIBO, including the C5—N6—C61—C62 and N6—C61—C62—C63 torsion angles as random variables, revealed more conformations in the same energy range due to the conformational flexibility of the side chain, but the same conformations of the diazepine ring were found. This conformational analysis shows that (*S*)-TIBO derivatives can adopt several low-energy conformations. In crystal structures of complexes of HIV-1 RT with TIBO analogues, one should examine very closely and carefully the electron density at the position of the bound inhibitor before a possible conformation of the TIBO is selected as a starting model.

Experimental

A sample of the title compound was obtained from the Janssen Research Foundation, Beerse, Belgium. The crystal used in the diffraction experiment was obtained by slow evaporation from a methanol solution at room temperature.

Crystal data

$C_{16}H_{21}ClN_3S^+\cdot Br^-\cdot CH_4O$
M_r = 434.82
Orthorhombic
$P2_12_12_1$
a = 7.498 (4) Å
b = 9.666 (5) Å
c = 28.04 (2) Å
V = 2032. (2) Å^3
Z = 4
D_x = 1.421 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections
θ = 10–11°
μ = 2.270 mm^{-1}
T = 293 K
Prism
0.70 × 0.50 × 0.30 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω scans
Absorption correction: ψ scan (*EMPIR*; Stoe & Cie, 1992*a*)
T_{min} = 0.245, T_{max} = 0.506
6506 measured reflections
2085 independent reflections (plus 1496 Friedel-related reflections)

2704 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.032
θ_{max} = 25°
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -33 \rightarrow 33$
3 standard reflections
frequency: 60 min
intensity decay: 50.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.108
S = 1.052
3581 reflections
222 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 1.2592P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (1)

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

C4—N3—C10b	124.7 (4)	N6—C7—C7a	114.8 (4)
N3—C4—C5	112.5 (4)	C7—C7a—C10b	121.2 (4)
C4—C5—N6	114.4 (3)	N3—C10b—C7a	129.1 (4)
C5—N6—C7	117.3 (3)		
C10b—N3—C4—C5	53.1 (6)	C5—N6—C61—C62	−168.9 (4)
C4—N3—C10b—C7a	−3.3 (8)	C5—N6—C7—C7a	−59.5 (5)
N3—C4—C5—C51	−163.3 (4)	C61—N6—C7—C7a	66.9 (5)
N3—C4—C5—N6	75.4 (5)	N6—C61—C62—C63	−138.7 (5)
C4—C5—N6—C61	−143.3 (4)	N6—C7—C7a—C10b	60.2 (6)
C4—C5—N6—C7	−14.2 (5)	C7—C7a—C10b—N3	−3.5 (8)
C51—C5—N6—C61	93.5 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br1	0.86	2.45	3.306 (4)	178
N6—H6···O71	0.91	1.89	2.763 (6)	161
O71—H71···Br1^{i}	0.82	2.41	3.201 (5)	164

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

During the data collection, the intensity of the check reflections gradually decreased to 50% of the initial values. The decay was corrected stepwise with a constant scale factor within each hourly interval. H atoms were positioned geometrically, and refined with a riding model and U_{iso} constrained to be 1.25U_{eq} of the carrier atom.

Data collection: *DIF*4 (Stoe & Cie, 1992*b*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*c*). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1419). Services for accessing these data are described at the back of the journal.

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2-Aminobenzimidazolium nitrate at 152 K, a triclinic crystal structure with pronounced local pseudo-symmetry

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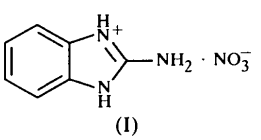
Abstract

The crystal structure of the title compound, $C_7H_8N_3^+\cdot NO_3^-$, contains four independent molecules. Molecules 1 and 2 are related by local pseudo $2_1/b$ symmetry (*a* axis unique). Molecules 3 and 4 are related by a local pseudo $2_1/a$ symmetry (*b* axis unique). The layer containing molecules 1 and 2 can be transformed to the layer containing molecules 3 and 4 by a rotation of 90° about a local axis perpendicular to the (001) plane plus a translation of *c*/2. The cations and anions are connected by hydrogen bonding to form flat ribbons.

Comment

The structure determination of the title compound, (I), is part of our study of possible hydrogen-bonding arrangements in guanidinium nitrate complexes (Schellhaas *et al.*, 1998). No other crystal structure containing a 2-aminobenzimidazolium group has been reported so far.



(I)

The asymmetric unit of (I) contains four independent molecules. The four aminobenzimidazole groups are almost planar. Individual atoms deviate less than 0.02 Å from the best plane through each group. The four independent nitrate groups are perfectly planar. The C—N_{amino} distances range from 1.309 (2) to 1.314 (2) Å and are slightly shorter than the adjacent C—N bonds in the imidazolium rings which range from 1.342 (2) to 1.348 (2) Å. Each cation donates four hydrogen bonds to three different nitrate groups. Each nitrate group accepts four hydrogen bonds from three different cations. The hydrogen bonding results in flat ribbon structures similar to those found in the crystal structure of *rac*-ptilocaulin nitrate (Schellhaas *et al.*, 1998). The ribbon containing molecules 1 and 2 (Fig. 1) connects these molecules in the crystallographic *a* direction. Adjacent parallel ribbons are related by crystallographic inversion centers to the stacks. Some O···O, O···N, O···C and N···C distances between adjacent ribbons are only 0.1 Å longer than the van der Waals contact distances. There are no short C···C contacts between adjacent ribbons. Thus $\pi\cdots\pi$ interactions in the stacks are not important.

The ribbon containing molecules 3 and 4 (Fig. 2) connects these molecules in the crystallographic *b* direction. Adjacent parallel ribbons are again related by crystallographic inversion centers. Similar stacks are observed as for molecules 1 and 2. Neighboring stacks are connected by benzene···benzene interactions (Fig. 3). These benzene groups show T-shaped arrangements. This has been shown to result in favorable electrostatic interactions (Koch & Egert, 1995).

The crystal structure of the title compound shows very pronounced pseudo-symmetry. A method to locate pseudo-symmetry elements in crystal structures has been described by Kálmán & Argay (1998). The pseudo-symmetry is best visualized using an orthogonal axes system which is approximately obtained by the axes transformation: $\mathbf{a}' = \mathbf{a}$, $\mathbf{b}' = \mathbf{b}$, $\mathbf{c}' = -[(c/a)\cos\beta]\mathbf{a} - [(c/b)\cos\alpha]\mathbf{b} + \mathbf{c}$. Then the fractional coordinates transform according to: $x' = x + [(c/a)\cos\beta]z$, $y' = y + [(c/b)\cos\alpha]z$, $z' = z$. After choosing the appropriate origin, molecule 2 can be transformed to molecule 1 by the pseudo-relation: $x_2 \simeq 0.50 - x_1$, $y_2 \simeq 0.50 + y_1$, $z_2 \simeq z_1$. This is a pseudo-glide plane perpendicular to the *a* axis with a translation of *b*/2 (*b*-glide). If this pseudo-glide plane is combined with the crystallographic inversion center at (0, 0, $\frac{1}{2}$) a new pseudo-symmetry relation is obtained (relation: $x_2 \simeq x_1 + 0.50$, $y_2 \simeq 0.50 - y_1$, $z_2 \simeq 1 - z_1$) which corresponds to a pseudo-screw axis in the crystallographic *a* direction. It is this pseudo-2_1-screw axis which connects the molecules within the hydrogen-bonded ribbon. Thus the layer containing molecules 1 and 2 has a pseudo-monoclinic structure belonging to structural class $P_{I(XY)}$ $2_1/b$ $Z = 4(1)$, using the notation of Zorky (1996). Molecule 4 can be transformed to molecule 3 by the pseudo-relation: $x_4 \simeq 0.50 + x_3$, $y_4 \simeq 0.50 - y_3$, $z_4 \simeq z_3$. This is a pseudo-glide plane