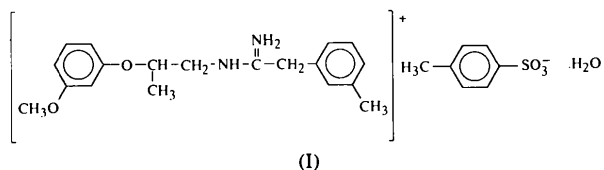


Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: AB1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



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N-[2-(3-Methoxyphenoxy)propyl]-*m*-tolyl-acetamidinium *p*-Toluenesulfonate Monohydrate (Xylamidine)[†]

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Abstract

The crystal structure of xylamidine, $C_{19}H_{25}N_2O_2^+ \cdot C_7H_7O_3S^- \cdot H_2O$, a peripheral 5-HT₂ receptor antagonist, is reported. The xylamidinium cation is folded with an almost parallel arrangement of the aromatic rings.

Comment

The crystal structure determination of xylamidine, (I), a peripheral 5-HT₂ receptor antagonist, forms part of our continuing work on serotonin antagonists (Blaton,

[†] Internal code of the Janssen Research Foundation: R13489.

Peeters & De Ranter, 1985, 1995, and references cited therein). The crystal determination showed rotational disorder of the *m*-tolyl moiety. The partial occupancies refined to 0.538 (7) for atoms C17–C23 and to 0.462 (7) for C117–C123, hereafter called conformations *A* and *B*, respectively. Fig. 1 shows the xylamidinium cation in the *A* conformation together with the water molecule and the *p*-toluenesulfonate anion. Neither the cation nor the anion exhibit any unusual bond lengths or angles. The xylamidinium cation is folded with an almost parallel arrangement of the aromatic rings [dihedral angles between the least-squares planes 4.0 (4) and 7.5 (4)° for conformations *A* and *B*, respectively]. The molecules are involved in a network of hydrogen bonds (Table 3) resulting in a double interconnected infinite chain of xylamidinium, H₂O and *p*-toluenesulfonate in the *a* direction.

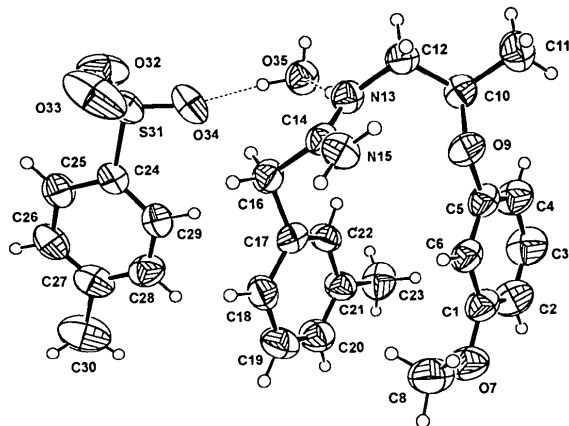


Fig. 1. Perspective view of the title compound in the *A* conformation with atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

Experimental

Crystal data

$C_{19}H_{25}N_2O_2^+ \cdot C_7H_7O_3S^- \cdot H_2O$
 $M_r = 502.61$
 Monoclinic
 $P2_1/n$
 $a = 8.217 (7) \text{ \AA}$
 $b = 31.54 (1) \text{ \AA}$
 $c = 10.384 (4) \text{ \AA}$
 $\beta = 98.09 (4)^\circ$

Cu $K\alpha$ radiation
 $\lambda = 1.54184 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 14\text{--}28^\circ$
 $\mu = 1.430 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Prism

$V = 2664. (3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.253 \text{ Mg m}^{-3}$
 $D_m = 1.24 \text{ Mg m}^{-3}$
 D_m measured by flotation in
n-heptane/CCl₄

$0.40 \times 0.40 \times 0.30 \text{ mm}$
 Colourless
 Crystal source: Janssen
 Research Foundation,
 Belgium

C122	-0.086 (3)	0.3609 (5)	0.497 (2)	0.071 (5)
C123	0.245 (1)	0.3073 (4)	0.814 (1)	0.153 (6)
C24	-0.4296 (3)	0.42390 (9)	0.8450 (2)	0.0604 (9)
C25	-0.4883 (4)	0.4270 (1)	0.9618 (3)	0.074 (1)
C26	-0.4664 (4)	0.3943 (1)	1.0492 (3)	0.086 (1)
C27	-0.3837 (5)	0.3582 (1)	1.0259 (4)	0.088 (1)
C28	-0.3224 (4)	0.3554 (1)	0.9090 (4)	0.089 (1)
C29	-0.3448 (4)	0.3877 (1)	0.8187 (3)	0.076 (1)
C30	-0.3598 (6)	0.3227 (1)	1.1238 (5)	0.137 (2)
S31	-0.46476 (9)	0.46493 (2)	0.73030 (7)	0.0721 (3)
O32	-0.6324 (3)	0.47677 (9)	0.7245 (3)	0.119 (1)
O33	-0.3524 (4)	0.4981 (1)	0.7690 (3)	0.142 (2)
O34	-0.4397 (4)	0.4469 (1)	0.6087 (2)	0.138 (1)
O35	-0.3977 (2)	0.42985 (6)	0.3620 (2)	0.0813 (8)

Data collection

Hilger & Watts four-circle
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 empirical (North, Phillips
 & Mathews, 1968)
 $T_{\min} = 0.870$, $T_{\max} =$
 0.995
 8051 measured reflections
 4789 independent reflections

3028 observed reflections
 $[F^2 > 3\sigma(F^2)]$
 $R_{\text{int}} = 0.0234$
 $\theta_{\max} = 70^\circ$
 $h = -9 \rightarrow 6$
 $k = 0 \rightarrow 38$
 $l = -12 \rightarrow 12$
 3 standard reflections
 monitored every 50
 reflections
 intensity decay: <2.0%

Refinement

Refinement on F^2
 $R[F^2 > 3\sigma(F^2)] = 0.0511$
 $wR(F^2) = 0.1389$
 $S = 1.078$
 4789 reflections
 386 parameters
 H-atom parameters not
 refined
 $w = 1/[\sigma^2(F_o^2) + (0.065P)^2$
 $+ 0.9039P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.041$
 $\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV, Tables
 2.2B, 2.3.1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

C1—C2	1.380 (5)	C20—C21	1.36 (2)
C1—C6	1.375 (4)	C21—C22	1.40 (2)
C1—O7	1.367 (4)	C21—C23	1.50 (1)
C2—C3	1.372 (6)	C117—C118	1.37 (3)
C3—C4	1.387 (5)	C117—C122	1.40 (2)
C4—C5	1.363 (4)	C118—C119	1.41 (2)
C5—C6	1.375 (4)	C119—C120	1.34 (2)
C5—O9	1.382 (3)	C119—C123	1.52 (2)
O7—C8	1.403 (5)	C120—C121	1.37 (2)
O9—C10	1.422 (3)	C121—C122	1.39 (2)
C10—C11	1.502 (5)	C24—C25	1.371 (4)
C10—C12	1.504 (4)	C24—C29	1.384 (4)
C12—N13	1.446 (4)	C24—S31	1.755 (3)
N13—C14	1.308 (3)	C25—C26	1.366 (5)
C14—N15	1.309 (4)	C26—C27	1.366 (5)
C14—C16	1.494 (4)	C27—C28	1.381 (6)
C16—C17	1.52 (1)	C27—C30	1.507 (6)
C16—C117	1.52 (1)	C28—C29	1.380 (5)
C17—C18	1.40 (2)	S31—O32	1.420 (3)
C17—C22	1.37 (2)	S31—O33	1.416 (3)
C18—C19	1.40 (2)	S31—O34	1.425 (3)
C19—C20	1.36 (2)		
C6—C1—O7	123.5 (3)	C20—C21—C22	117 (1)
C2—C1—O7	116.3 (3)	C22—C21—C23	120 (1)
C2—C1—C6	120.1 (3)	C17—C22—C21	123 (1)
C1—C2—C3	118.8 (3)	C16—C117—C122	121 (1)
C2—C3—C4	121.5 (4)	C16—C117—C118	118 (1)
C3—C4—C5	118.6 (3)	C118—C117—C122	118 (1)
C4—C5—O9	124.5 (3)	C117—C118—C119	122 (2)
C4—C5—C6	120.8 (3)	C118—C119—C123	121 (1)
C6—C5—O9	114.6 (3)	C118—C119—C120	117 (2)
C1—C6—C5	120.1 (3)	C120—C119—C123	121 (1)
C1—O7—C8	117.2 (3)	C119—C120—C121	122 (1)
C5—O9—C10	119.8 (2)	C120—C121—C122	120 (1)
O9—C10—C12	105.7 (3)	C117—C122—C121	119 (2)
O9—C10—C11	110.4 (3)	C29—C24—S31	120.9 (2)
C11—C10—C12	111.4 (3)	C25—C24—S31	120.3 (2)
C10—C12—N13	112.7 (2)	C25—C24—C29	118.8 (3)
C12—N13—C14	126.1 (3)	C24—C25—C26	120.3 (3)
N13—C14—C16	118.5 (3)	C25—C26—C27	122.2 (3)
N13—C14—N15	123.3 (3)	C26—C27—C30	121.5 (4)
N15—C14—C16	118.2 (3)	C26—C27—C28	117.5 (3)
C14—C16—C17	110.8 (5)	C28—C27—C30	121.0 (4)
C14—C16—C117	114.8 (6)	C27—C28—C29	121.3 (3)
C16—C17—C22	119 (1)	C24—C29—C28	119.9 (3)
C16—C17—C18	119.9 (9)	C24—S31—O34	106.1 (2)
C18—C17—C22	117 (1)	C24—S31—O33	108.3 (2)
C17—C18—C19	119 (1)	C24—S31—O32	106.8 (2)
C18—C19—C20	120 (1)	O33—S31—O34	112.1 (2)
C19—C20—C21	122 (1)	O32—S31—O34	109.1 (3)
C20—C21—C23	123 (1)	O32—S31—O33	114.1 (2)
C6—C1—O7—C8	1.5 (5)	C12—N13—C14—N15	3.9 (5)
C4—C5—O9—C10	25.1 (5)	C12—N13—C14—C16	-177.0 (3)
C6—C5—O9—C10	-156.6 (3)	N13—C14—C16—C17	99.2 (7)
C5—O9—C10—C11	-99.6 (3)	C14—C16—C17—C18	127 (1)
C5—O9—C10—C12	139.8 (3)	C14—C16—C117—C118	109 (1)
O9—C10—C12—N13	-59.5 (3)	C29—C24—S31—O32	134.1 (3)
C11—C10—C12—N13	-179.4 (3)	C29—C24—S31—O33	-102.6 (3)
C10—C12—N13—C14	90.4 (4)	C29—C24—S31—O34	17.9 (3)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
C1	0.3115 (4)	0.30818 (9)	0.3462 (3)	0.078 (1)
C2	0.2367 (5)	0.2786 (1)	0.2593 (4)	0.106 (2)
C3	0.1287 (6)	0.2924 (1)	0.1548 (5)	0.112 (2)
C4	0.0950 (5)	0.3351 (1)	0.1341 (4)	0.093 (1)
C5	0.1709 (4)	0.36376 (8)	0.2209 (3)	0.068 (1)
C6	0.2789 (4)	0.35064 (8)	0.3267 (3)	0.068 (1)
O7	0.4176 (3)	0.29269 (7)	0.4486 (3)	0.104 (1)
C8	0.4929 (5)	0.3222 (1)	0.5391 (4)	0.110 (2)
O9	0.1516 (2)	0.40721 (5)	0.2101 (2)	0.0712 (8)
C10	0.0060 (4)	0.42435 (9)	0.1389 (3)	0.067 (1)
C11	0.0358 (5)	0.4371 (1)	0.0048 (3)	0.093 (1)
C12	-0.0379 (3)	0.46199 (8)	0.2160 (3)	0.062 (1)
N13	-0.0656 (3)	0.45076 (7)	0.3461 (2)	0.0607 (8)
C14	0.0454 (3)	0.45007 (7)	0.4496 (3)	0.0572 (9)
N15	0.1979 (3)	0.46199 (7)	0.4492 (2)	0.0653 (8)
C16	-0.0046 (4)	0.43551 (8)	0.5753 (3)	0.066 (1)
C17	0.044 (2)	0.3894 (3)	0.602 (2)	0.053 (3)
C18	0.136 (3)	0.3781 (5)	0.721 (1)	0.072 (3)
C19	0.161 (2)	0.3352 (5)	0.752 (1)	0.090 (4)
C20	0.082 (2)	0.3049 (4)	0.672 (1)	0.087 (5)
C21	-0.017 (2)	0.3147 (4)	0.560 (1)	0.072 (4)
C22	-0.043 (2)	0.3578 (4)	0.532 (1)	0.067 (4)
C23	-0.0959 (9)	0.2818 (2)	0.4670 (7)	0.101 (3)
C117	-0.006 (2)	0.3876 (4)	0.593 (2)	0.052 (4)
C118	0.114 (3)	0.3703 (5)	0.683 (2)	0.075 (4)
C119	0.126 (3)	0.3261 (5)	0.703 (2)	0.092 (6)
C120	0.033 (2)	0.3012 (4)	0.617 (2)	0.091 (6)
C121	-0.072 (2)	0.3174 (4)	0.514 (1)	0.083 (5)

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

D—H...A	D—H	H...A	D...A	D—H...A
N13—H13...O35	0.860	1.977	2.834 (4)	174.3
O35—H1W...O34	0.948	1.743	2.688 (3)	174.3
N15—H15A...O33 ⁱ	0.860	2.181	3.023 (4)	166.2
O35—H2W...O32 ⁱⁱ	0.833	2.352	3.099 (4)	149.4
O35—H2W...O33 ⁱⁱⁱ	0.833	2.525	3.232 (4)	143.3
N15—H15B...O32 ⁱⁱⁱ	0.860	2.227	3.035 (4)	156.4
N15—H15B...O34 ⁱⁱⁱ	0.860	2.499	3.232 (5)	143.6

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

The data were collected using a fixed scan speed of $1.2^\circ \text{ min}^{-1}$ and a scan width of 1.2° . The structure was solved by a combination of Patterson and direct methods on the difference structure. Refinement was performed with full-matrix least-squares on F^2 for all reflections. The sum of the occupation factors of the disordered *m*-tolyl moiety was constrained to 1.0. The ring distances of these moieties were tied to a free variable and restrained to vary within 0.03 Å. Adjacent non-H atoms were restrained to have the same U_{ij} components within 0.01 \AA^2 . H atoms were calculated at geometrical positions and allowed to ride on their parent atoms.

Data collection: Hilger & Watts Y290 software. Cell refinement: XRAY76 PARAM (Stewart *et al.*, 1976). Data reduction: REDU4 (Stoe & Cie, 1992). Program(s) used to solve structure: DIRDIF (Beurskens *et al.*, 1981). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEX2.1b (McArdle, 1994). Software used to prepare material for publication: PARST (Nardelli, 1983).

The authors thank Dr Jan Tollenaere of Janssen Research Foundation, Beerse, Belgium, for the provision of a sample of the title compound.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1140). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 993–995

tert-Butyl 2-[(Hydroxy)(5-hydroxy-1,3-benzodioxol-6-yl)methyl]pyrrolidine-1-carboxylate

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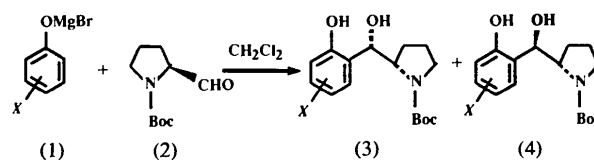
(Received 19 March 1993; accepted 4 October 1994)

Abstract

The title compound, $\text{C}_{17}\text{H}_{23}\text{NO}_6$, was prepared from a phenoxymagnesium bromide derivative and *N*-*tert*-butoxycarbonyl-L-prolinal in a chemical reaction which is an example of controlled α -chelation. The structure of the compound elucidates the chemical pathway of the synthesis process.

Comment

Ephedrine-like compounds have been obtained with good to excellent diastereoselection (Bigi, Casnati, Sartori, Araldi & Bocelli, 1989; Bigi, Casnati, Sartori & Araldi, 1990) *via* coordinated Friedel–Crafts alkylation of phenols. In particular, the reaction at room temperature of phenoxymagnesium bromide derivatives (1) with *N*-*tert*-butoxycarbonyl-L-prolinal, (2) (Boc = *tert*-butoxycarbonyl), gives the 2-hydroxy- α -[1-(*tert*-butoxycarbonylamino)-2-pyrrolidinyl]benzenemethanol derivatives (3) and (4) in good yields and with excellent diastereoselectivity (d.e. > 94%).



This general approach to the synthesis of chiral β -amino-*ortho*-hydroxybenzyl alcohols *via* direct *ortho*-hydroxyalkylation of phenol rings at room temperature with good yields and good diastereoselectivity has already been used with different *N*-(Boc)- α -