Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.104$
$S = 0.905$
3274 reflections
238 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0574P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.182$ e Å^{-3}
$\Delta\rho_{min} = -0.172$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.0069 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C12	1.359 (2)	C11—C21	1.497 (2)
O2—C22	1.356 (2)	C31—C41	1.480 (2)
O1—C12—C11	118.11 (16)	O2—C22—C23	121.90 (17)
O1—C12—C13	121.69 (18)	C33—N34—C35	116.02 (18)
O2—C22—C21	117.91 (16)	C43—N44—C45	116.02 (17)
C16—C11—C21—C26	−124.4 (2)	C36—C31—C41—C42	21.2 (3)
C12—C11—C21—C26	55.6 (2)	C32—C31—C41—C42	−162.8 (2)
C16—C11—C21—C22	55.2 (2)	C36—C31—C41—C46	−156.7 (2)
C12—C11—C21—C22	−124.8 (2)	C32—C31—C41—C46	19.3 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N34	0.82	1.98	2.793 (3)	172
O2—H2···N44'	0.82	1.96	2.750 (3)	161

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

Compound (I) crystallized in the monoclinic system. From the systematic absences, the space group was $P2_1/n$. H atoms were treated as riding atoms (C—H 0.93 and O—H 0.82 Å).

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* (*CAD*-4-*PC Software*; Enraf–Nonius, 1992). Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

We thank Dr J. F. Gallagher and Dublin City University for the funds to purchase the X-ray tube used in the data collections. While no direct support for the research described here was provided by NSERC (Canada), we do thank that organization for the partial funding of the 1992 upgrade of the CAD-4 diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1245). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Coupar, P. I., Glidewell, C. & Ferguson, G. (1997). *Acta Cryst.* B**53**, 521–533.

Enraf–Nonius (1992). *CAD*-4-*PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G. (1998). *PREP8. A WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL97 Programs*. University of Guelph, Canada.

Ferguson, G., Bell, W., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 534–543.

Ferguson, G., Coupar, P. I. & Glidewell, C. (1997). *Acta Cryst.* B**53**, 513–520.

Ferguson, G., Glidewell, C., Gregson, R. M., Meehan, P. R. & Patterson, I. L. J. (1998). *Acta Cryst.* B**54**, 151–161.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Sheldrick, G. M. (1997*a*). *SHELXL*97. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1997*b*). *SHELXS*97. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1998). *PLATON. Molecular Geometry and Graphics Program*. June 1998 version. University of Utrecht, The Netherlands.

Acta Cryst. (1999). C**55**, 432–434

Paroxetine hydrochloride hemihydrate

James A. Ibers

Department of Chemistry, Northwestern University, Evanston, IL 60208-3113, USA. E-mail: ibers@chem.nwu.edu

(*Received 23 July 1998; accepted 15 October 1998*)

Abstract

The structure of the title compound {systematic name: (3*S*-*trans*)-3-[(1,3-benzodioxol-5-yloxy)methyl]-4-(4-fluorophenyl)piperidinium chloride hemihydrate, $C_{19}H_{21}FNO_3^+\cdot Cl^-\cdot 0.5H_2O$}, comprises two piperidinium cations (*A* and *B*), two chloride anions, and one water molecule in the asymmetric unit. A piperidinium proton of cation *A* is hydrogen bonded to the water molecule. The second proton points in the direction of one chloride anion, as does a piperidinium proton of cation *B*. One water proton points in the direction of another chloride anion.

Comment

Paroxetine hydrochloride hemihydrate is a serotonin (5-HT) uptake inhibitor and is of therapeutic use as an antidepressant (Barnes *et al.*, 1988). There is increased interest in the use of paroxetine as an alternative to the benzodiazepines in the treatment of generalized anxiety disorder (Rocca *et al.*, 1997). Paroxetine hydrochloride hemihydrate, (I), can be dehydrated, although the hemihydrate is more stable (Buxton *et al.*, 1988). Recently, a variety of 'anhydrates' have been reported

Acta Crystallographica Section C
ISSN 0108-2701 © 1999

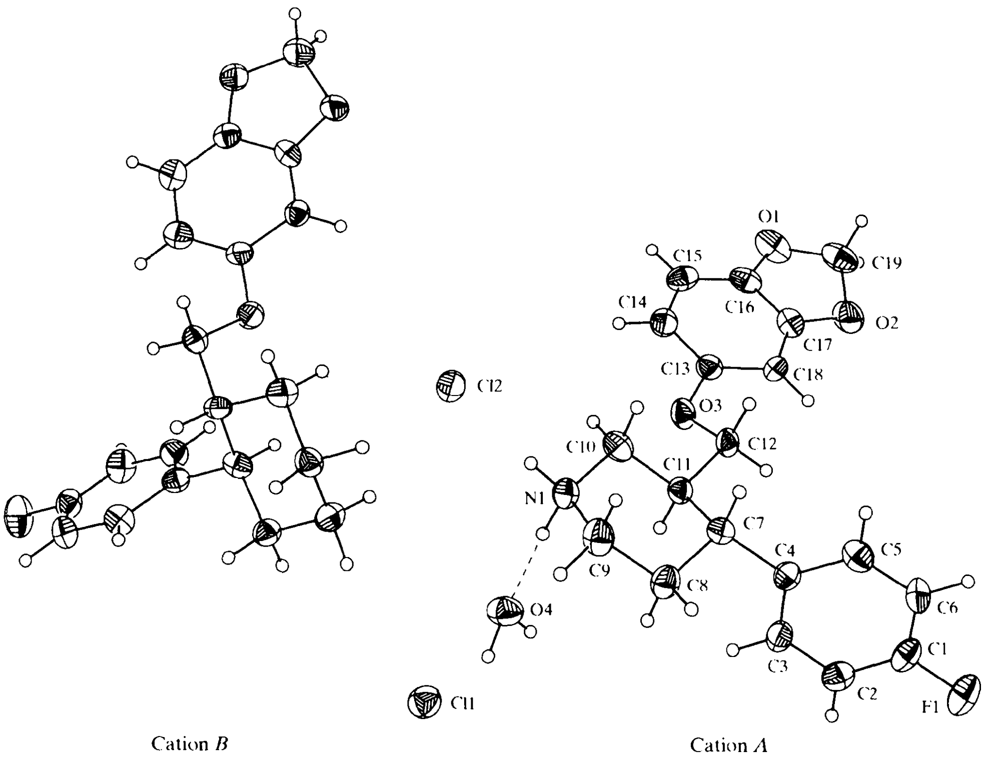
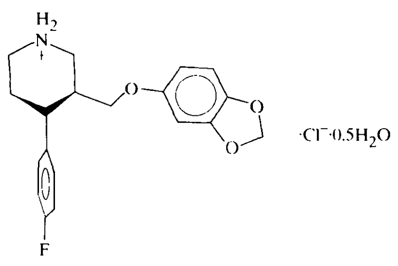


Fig. 1. The structure of paroxetine hydrochloride hemihydrate with 50% probability displacement ellipsoids, except for H atoms, which are drawn as small circles.

(Jacewicz & Ward, 1996), but these have not been characterized structurally. We report here the first crystal structure of a paroxetine hydrochloride compound.



(I)

The structure of the hemihydrate (I) confirms the basic composition and stereochemistry of paroxetine, as derived by spectroscopic and chemical means. The water molecule is bound to one of the paroxetine molecules through an N—H···O hydrogen bond 2.772 (6) Å in length. That paroxetine hydrochloride hemihydrate is readily dehydrated is thus not surprising.

Experimental

The title compound was obtained from Schein Pharmaceutical, Danbury, Connecticut, USA.

Crystal data

$C_{19}H_{21}FNO_3^+ \cdot Cl^- \cdot 0.5H_2O$
$M_r = 374.83$
Monoclinic
$P2_1$
$a = 12.8953\ (17)$ Å
$b = 10.0927\ (11)$ Å
$c = 14.413\ (2)$ Å
$\beta = 106.638\ (12)°$
$V = 1797.2\ (4)$ Å^3
$Z = 4$
$D_x = 1.385$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 1828 reflections
$\theta = 1–25°$
$\mu = 0.244$ mm^{-1}
$T = 153\ (2)$ K
Needle
0.29 × 0.076 × 0.044 mm
Colourless

Data collection

Bruker Smart 1000 CCD diffractometer
ω scans
Absorption correction: numerical, face indexed (Sheldrick, 1997)
$T_{min} = 0.954$, $T_{max} = 0.991$
10 872 measured reflections
6093 independent reflections

3802 reflections with $I > 2\sigma(I)$
$R_{int} = 0.065$
$\theta_{max} = 25°$
$h = -15 \rightarrow 15$
$k = -11 \rightarrow 12$
$l = -17 \rightarrow 15$
Intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.044$
$wR(F^2) = 0.089$

$(\Delta/\sigma)_{max} = 0.014$
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

$S = 0.78$
6093 reflections
484 parameters
H atoms treated by a mixture of independent and constrained refinement
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.06 (6)

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

C1*A*—F1*A*	1.365 (5)	C16*A*—C17*A*	1.368 (6)
C1*B*—F1*B*	1.366 (5)	C16*A*—O1*A*	1.384 (5)
C4*A*—C7*A*	1.518 (6)	C16*B*—C17*B*	1.383 (6)
C4*B*—C7*B*	1.518 (5)	C16*B*—O1*B*	1.392 (5)
C7*A*—C11*A*	1.537 (5)	C17*A*—O2*A*	1.375 (5)
C7*A*—C8*A*	1.541 (5)	C17*B*—O2*B*	1.370 (4)
C7*B*—C8*B*	1.538 (5)	C19*A*—O1*A*	1.417 (6)
C7*B*—C11*B*	1.539 (5)	C19*A*—O2*A*	1.445 (5)
C8*A*—C9*A*	1.517 (6)	C19*B*—O2*B*	1.418 (5)
C8*B*—C9*B*	1.516 (5)	C19*B*—O1*B*	1.452 (5)
C9*A*—N1*A*	1.496 (5)	Cl1···H1O4^{i}	2.35 (5)
C9*B*—N1*B*	1.490 (5)	Cl2···H2N2	1.94 (5)
C10*A*—N1*A*	1.475 (5)	Cl2···H1N1	2.18 (4)
C10*A*—C11*A*	1.523 (6)	N1*A*—H1N1	0.89 (4)
C10*B*—N1*B*	1.483 (5)	N1*A*—H2N1	1.12 (5)
C10*B*—C11*B*	1.542 (5)	N1*B*—H1N2	0.84 (4)
C11*A*—C12*A*	1.524 (5)	N1*B*—H2N2	1.22 (5)
C11*B*—C12*B*	1.501 (5)	O4—H1O4	0.79 (5)
C12*A*—O3*A*	1.428 (4)	O4—H2O4	0.99 (7)
C12*B*—O3*B*	1.428 (4)	O4···H2N1	1.69 (5)
C13*A*—O3*A*	1.381 (4)	O4···N1*A*	2.772 (6)
C13*B*—O3*B*	1.371 (4)		
C4*A*—C7*A*—C11*A*	114.5 (4)	C16*A*—C17*A*—O2*A*	110.0 (4)
C4*A*—C7*A*—C8*A*	111.3 (3)	C18*A*—C17*A*—O2*A*	127.1 (4)
C4*B*—C7*B*—C8*B*	112.5 (3)	O2*B*—C17*B*—C18*B*	128.3 (4)
C4*B*—C7*B*—C11*B*	109.7 (3)	O2*B*—C17*B*—C16*B*	109.9 (3)
O3*A*—C12*A*—C11*A*	105.8 (3)	O1*A*—C19*A*—O2*A*	107.2 (4)
O3*B*—C12*B*—C11*B*	108.7 (3)	O2*B*—C19*B*—O1*B*	107.0 (3)
O3*A*—C13*A*—C14*A*	115.7 (4)	H1N1—N1*A*—H2N1	112 (4)
O3*A*—C13*A*—C18*A*	122.8 (4)	H1N2—N1*B*—H2N2	114 (4)
O3*B*—C13*B*—C14*B*	123.3 (4)	H1O4—O4—H2O4	94 (5)
O3*B*—C13*B*—C18*B*	115.2 (4)	N1*A*—H1N1···Cl2	174 (4)
C15*A*—C16*A*—O1*A*	128.4 (4)	N1*A*—H2N1···O4	159 (4)
C17*A*—C16*A*—O1*A*	109.7 (4)	N1*B*—H2N2···Cl2	152 (3)
C15*B*—C16*B*—O1*B*	128.7 (4)	O4—H1O4···Cl1^{ii}	164 (4)
C17*B*—C16*B*—O1*B*	109.2 (4)	O4—H2O4···Cl1	143 (6)

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

The positional and isotropic displacement parameters of the H atoms on the piperidinium N atoms and on the water molecule were refined. Other H atoms were placed at calculated positions and were refined with a riding model. All non-H atoms were refined anisotropically.

Data collection: *SMART* (Bruker, 1997). Cell refinement: *SMART*. Data reduction: *SAINT-Plus* (Bruker, 1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

I thank Schein Pharmaceutical, Danbury, Connecticut, USA, for the sample of the title compound and Christopher Pernin and Paul Jene for assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1162). Services for accessing these data are described at the back of the journal.

References

Barnes, R. D., Wood-Kaczmar, M. W., Curzons, A. D., Lynch, I. R., Richardson, J. E. & Buxton, P. C. (1988). US Patent No. 4 721 723.
Bruker (1997). *SMART* (Version 5.101) and *SAINT-Plus* (Version 5.101). *Data Collection and Processing Software for the SMART System*. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Buxton, P. C., Lynch, I. R. & Roe, J. M. (1988). *Int. J. Pharm.* **42**, 135–143.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Jacewicz, V. W. & Ward, N. (1996). Can. Patent Appl. 2 168 829.
Rocca, P., Fonzon, V., Scotta, M., Zanalda, E. & Ravizza, L. (1997). *Acta Psychiatr. Scand.* **95**, 444–450.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXTL/PC*. Version 5.101. *An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1999). C**55**, 434–436

Fromm's methylphenyldithiodimethylketuret

JOHN S. DAVIDSON,[a] STEVEN J. RETTIG[b] AND JAMES TROTTER[b]

[a]*Crosslaw, Ballplay Road, Moffat, Dumfriesshire DG10 9JU, Scotland, and* [b]*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1. E-mail: jtrt@xray4.chem.ubc.ca*

(*Received 9 July 1998; accepted 15 October 1998*)

Abstract

The 'keturet' obtained by reacting 1-methyl-1-phenyldithiobiuret with acetone is shown to be 6,6-dimethyl-2-methylanilino-5,6-dihydro-4*H*-1,3,5-thiadiazine-4-thione, $C_{12}H_{15}N_3S_2$. The molecule contains a six-membered thiadiazine ring with a distorted half-chair conformation, rather than a previously proposed four-membered ring structure. Molecular dimensions are normal, and the molecules (two per asymmetric unit) are linked by two N—H···S hydrogen bonds, one fairly strong [H···S 2.39 (3) Å] and one weaker [H···S 2.65 (4) Å].

Comment

Condensation of 1-aryldithiobiurets with ketones, under the influence of dry hydrogen chloride, gives compounds called 'keturets' (Fromm, 1893), some of which can be formulated as hexahydrotriazine derivatives (Fairfull & Peak, 1955). Reaction of 1-methyl-1-phenyldithiobiuret, (I), with acetone gives a keturet which cannot be a hexahydrotriazine (since the disubstitution on N1

Acta Crystallographica Section C
ISSN 0108-2701 © 1999