Refinement

Refinement on F
$R = 0.0585$
$wR = 0.0672$
$S = 1.584$
1421 reflections
209 parameters
H atoms not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.0056$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: Zachariasen (1968) type 2, Gaussian isotropic
Extinction coefficient: 3.60273
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Bond lengths (Å)*

O(1)—C(13)	1.233 (5)	C(6)—C(7)	1.530 (7)
O(2)—C(3)	1.429 (6)	C(7)—C(8)	1.519 (7)
O(3)—C(4)	1.452 (5)	C(8)—C(9)	1.328 (7)
O(3)—C(7)	1.429 (5)	C(8)—C(17)	1.506 (8)
C(1)—C(2)	1.530 (6)	C(9)—C(10)	1.511 (7)
C(1)—C(11)	1.579 (6)	C(10)—C(11)	1.566 (7)
C(1)—C(14)	1.532 (7)	C(11)—C(12)	1.530 (6)
C(1)—C(15)	1.531 (7)	C(12)—C(13)	1.471 (6)
C(2)—C(3)	1.537 (7)	C(12)—C(18)	1.351 (6)
C(3)—C(4)	1.542 (7)	C(13)—C(14)	1.511 (7)
C(4)—C(5)	1.543 (7)	C(18)—C(19)	1.495 (7)
C(4)—C(16)	1.512 (7)	C(18)—C(20)	1.520 (7)
C(5)—C(6)	1.507 (7)		

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992). Cell refinement: *CAD-4-PC Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: HA1168). 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. (1997). C**53**, 313–315

(±)-2-[Hydroxy(4-methoxyphenyl)methyl]-2*H*-1,4-benzothiazin-3(4*H*)-one Hydrate

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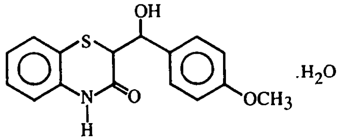
Abstract

The title compound, $C_{16}H_{15}NO_3S.H_2O$, is a derivative of benzothiazine. The molecular packing is stabilized by a three-dimensional hydrogen-bonding network. The benzothiazine ring is distorted, showing a half-chair conformation. The benzene ring is planar, but the methoxy group deviates significantly from planarity. A pair of intermolecular hydrogen bonds forms a centrosymmetric dimer in the crystal. There are intermolecular hydrogen bonds with a water molecule. The hydroxy(4-methoxyphenyl)methyl group and carbonyl O(20) atom are pseudo-equatorial with respect to the benzothiazine ring.

Comment

The title compound, (I), is a derivative of benzothiazine. This class of compounds possess potent Ca^{2+} antagonist activity, which is an important pharmacological activity (Ota, Ito & Kawashima, 1992), but the pharmacological action of (I) is unknown. In order to study the structure and geometrical conformation of the benzothiazine ring and its substituents, the X-ray analysis of (I) has been carried out.



(I)

The molecular structure of (I) is shown in Fig. 1. The interatomic distances and angles in the 1,4-benzothiazine ring are in agreement with the given atom type, hybridization and requirement of six-membered-ring geometry. The S—C bond lengths are not equal

[S(7)—C(2) 1.758 (3) and S(7)—C(8) 1.804 (4) Å]. One of them is shortened due to the conjugation of the π-electron system. The C—N distances are also unequal [C(3)—N(21) 1.402 (4) and C(19)—N(21) 1.337 (4) Å] owing to differing environments. The S—C and C—N distances in (I) are shorter compared with the 1,5-benzothiazepine ring (Kojic-Prodic, Ruzic-Toros & Sunjic, 1984; Kumaradhas, Nirmala & Ravikumar, 1995; Kumaradhas & Nirmala, 1997) due to higher binding in the benzothiazine ring and compared with the phenolthiazine ring (McDowell, 1976), the S—C and C—N distances are comparable. The bond lengths involving C_{sp^3} atoms range from 1.418 (4) to 1.514 (4) Å. The C—O bond lengths fall into three categories: C_{sp^3}—O single bond [C(18)—O(17) 1.429 (5) Å], C_{aryl}—O single bond [C(14)—O(17) 1.375 (3) Å] and C_{sp^2}=O double bond [C(19)—O(20) 1.234 (4) Å].

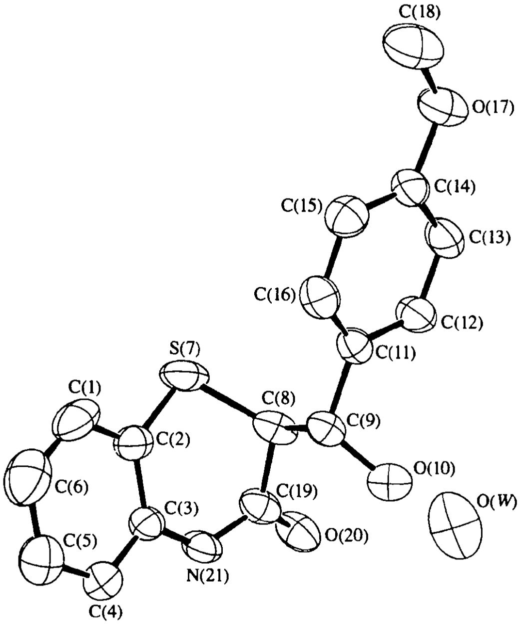


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The values of the torsion angles of the benzothiazine ring reflect a half-chair conformation (Hendrickson, 1961). The hydroxy(4-methoxyphenyl)methyl group and carbonyl O(20) atom at C(8) and C(19), respectively, are *trans* oriented as the C(9)—C(8)—C(19)—O(20) torsion angle of −98.9 (4)° shows. The conformation of the benzothiazine ring is determined by considering least-squares plane deviations: C(2), C(3) and C(8) lie 0.253 (4), 0.125 (3) and 0.563 (4) Å, respectively, above S(7) [−0.080 (1) Å], with N(21) and C(19) lying 0.218 (3) and 0.218 (4) Å, respectively, below the ring plane. The benzene ring is planar but the methoxyphenyl group deviates significantly from planarity. The dihedral angle between the benzothiazine ring and the hydroxy(4-methoxyphenyl)methyl group is 21.04 (7)°. The plane containing atoms O(20), C(19), C(8) and N(21) forms a dihedral angle of 27.04 (10)° with the benzothiazine ring. The hydroxy(4-methoxyphenyl)methyl group and carbonyl O(20) atom adopt a pseudo-equatorial position in the molecule.

The molecular packing is depicted in Fig. 2. The molecular packing is stabilized by a three-dimensional hydrogen-bonding network. The amide group hydrogen bond (N—H···O) forms a centrosymmetric dimer in the crystal with the adjacent molecule, as shown in Fig. 2. This is the important facet of the molecular packing. The water molecule forms O—H···O intermolecular hydrogen bonds (see Table 2). On the whole, the crystal packing is stabilized by hydrogen bonding with polar groups and van der Waals interactions with non-polar groups.

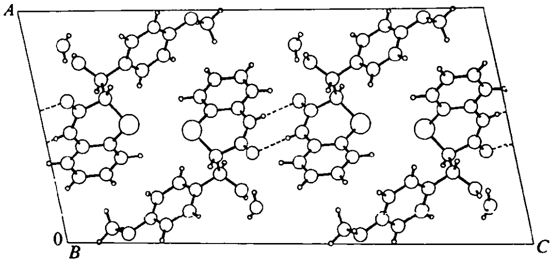


Fig. 2. Packing diagram of (I) viewed down the *b* axis. The N—H···O hydrogen bonds are shown, but the O—H···O hydrogen bonds are not.

Experimental

The title compound was recrystallized from ethanol at room temperature.

Crystal data

$C_{16}H_{15}NO_3S.H_2O$
$M_r = 319.37$
Monoclinic
$P2_1/c$
$a = 12.050 (6)$ Å
$b = 5.612 (2)$ Å
$c = 23.795 (4)$ Å
$\beta = 102.46 (2)°$
$V = 1571.2 (9)$ Å^3
$Z = 4$
$D_x = 1.350$ Mg m^{-3}
$D_m = 1.345$ Mg m^{-3}
D_m measured by flotation in a xylene–CCl_4 mixture

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 8–14°$
$\mu = 0.223$ mm^{-1}
$T = 294$ K
Needle
0.20 × 0.18 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none

$\theta_{max} = 25°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 28$

2375 measured reflections
2375 independent reflections
1578 reflections with
$I > 2\sigma(I)$
2 standard reflections
frequency: 60 min
intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.050$
$wR(F^2) = 0.094$
$S = 1.13$
2375 reflections
267 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.729P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}
Extinction correction: none
Scattering factors from
*SHELXL*93 (Sheldrick, 1993)

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

C(1)—C(6)	1.368 (6)	C(9)—C(11)	1.510 (4)
C(1)—C(2)	1.387 (5)	C(11)—C(16)	1.378 (4)
C(2)—C(3)	1.391 (4)	C(11)—C(12)	1.380 (4)
C(2)—S(7)	1.758 (3)	C(12)—C(13)	1.378 (4)
C(3)—C(4)	1.374 (4)	C(13)—C(14)	1.376 (4)
C(3)—N(21)	1.402 (4)	C(14)—C(15)	1.375 (4)
C(4)—C(5)	1.375 (5)	C(14)—O(17)	1.375 (3)
C(5)—C(6)	1.374 (5)	C(15)—C(16)	1.382 (4)
C(8)—C(19)	1.514 (4)	C(18)—O(17)	1.429 (5)
C(8)—C(9)	1.543 (4)	C(19)—O(20)	1.234 (4)
C(8)—S(7)	1.804 (4)	C(19)—N(21)	1.337 (4)
C(9)—O(10)	1.418 (4)		
C(6)—C(1)—C(2)	120.9 (3)	C(16)—C(11)—C(12)	117.8 (3)
C(1)—C(2)—C(3)	118.6 (3)	C(16)—C(11)—C(9)	121.6 (3)
C(1)—C(2)—S(7)	121.7 (3)	C(12)—C(11)—C(9)	120.7 (3)
C(3)—C(2)—S(7)	119.7 (3)	C(13)—C(12)—C(11)	121.5 (3)
C(4)—C(3)—C(2)	119.9 (3)	C(14)—C(13)—C(12)	119.6 (3)
C(4)—C(3)—N(21)	119.4 (3)	C(15)—C(14)—O(17)	124.1 (3)
C(2)—C(3)—N(21)	120.7 (3)	C(15)—C(14)—C(13)	120.2 (3)
C(3)—C(4)—C(5)	120.9 (3)	O(17)—C(14)—C(13)	115.7 (3)
C(6)—C(5)—C(4)	119.5 (4)	C(14)—C(15)—C(16)	119.2 (3)
C(1)—C(6)—C(5)	120.2 (4)	C(11)—C(16)—C(15)	121.8 (3)
C(19)—C(8)—C(9)	113.0 (3)	O(20)—C(19)—N(21)	121.8 (3)
C(19)—C(8)—S(7)	110.2 (2)	O(20)—C(19)—C(8)	121.2 (3)
C(9)—C(8)—S(7)	111.8 (2)	N(21)—C(19)—C(8)	117.1 (3)
O(10)—C(9)—C(11)	112.1 (2)	C(19)—N(21)—C(3)	127.7 (3)
O(10)—C(9)—C(8)	105.5 (3)	C(14)—O(17)—C(18)	118.0 (3)
C(11)—C(9)—C(8)	110.8 (2)	C(2)—S(7)—C(8)	97.7 (2)

S(7)—C(2)—C(3)—N(21)	2.4 (4)
S(7)—C(8)—C(9)—O(10)	172.1 (2)
C(19)—C(8)—C(9)—C(11)	168.7 (3)
C(9)—C(8)—C(19)—O(20)	−98.9 (4)
S(7)—C(8)—C(19)—N(21)	−45.1 (4)
C(8)—C(19)—N(21)—C(3)	4.5 (5)
C(2)—C(3)—N(21)—C(19)	20.3 (5)
C(3)—C(2)—S(7)—C(8)	−35.7 (3)
C(19)—C(8)—S(7)—C(2)	54.7 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N(21)—H(21)···O(20^{i})	0.81 (3)	2.09 (3)	2.903 (3)	177 (3)
O(10)—H(10)···O(*W*)	0.85 (4)	1.93 (4)	2.763 (5)	169 (3)
O(*W*)—H(*W*1)···O(20^{ii})	0.87 (6)	2.04 (5)	2.863 (5)	157 (5)

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

All non-H atoms were found by direct methods and the parameters were refined successfully with a full-matrix least-squares refinement procedure. H atoms were located on a difference Fourier map and included in the refinement, the refined H atoms having the bond lengths C—H 0.91–1.01 (5), N—H 0.81 (3) and O—H 0.74–0.87 (4) Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *DATRD*2 in *NRCVAX* (Gabe, Le Page, White & Lee, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*. Software used to prepare material for publication: *SHELXL*93.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1267). 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. (1997). C**53**, 315–318

(±)-*trans*-3-Hydroxy-2-(4-methoxyphenyl)-4-oxo-2,3,4,5-tetrahydro-1,5-benzothiazepine 1-Oxide

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Abstract

The title compound, $C_{16}H_{15}NO_4S$, is a drug intermediate of diltiazem. The molecular packing is stabilized by hydrogen bonding. The seven-membered ring is dis-