

C(4B)	-0.0535 (7)	0.3290 (5)	0.0978 (4)	0.031 (2)
C(5B)	-0.1733 (6)	0.3504 (5)	0.0731 (4)	0.0277 (15)
C(6B)	-0.2722 (7)	0.2818 (5)	0.0841 (4)	0.035 (2)
O(6B)	-0.3847 (4)	0.2913 (4)	0.0692 (3)	0.0460 (14)
N(7B)	-0.1806 (6)	0.4435 (5)	0.0399 (4)	0.0372 (14)
C(8B)	-0.0640 (7)	0.4749 (5)	0.0439 (4)	0.034 (2)
N(9B)	0.0183 (5)	0.4093 (4)	0.0791 (3)	0.0290 (13)
C(1'B)	0.1502 (6)	0.4293 (5)	0.0962 (4)	0.0288 (15)
C(2'B)	0.1799 (6)	0.4352 (5)	0.1856 (4)	0.031 (2)
O(2'B)	0.1495 (4)	0.5255 (4)	0.2210 (3)	0.0417 (13)
C(3'B)	0.3200 (6)	0.4098 (5)	0.1849 (4)	0.030 (2)
O(3'B)	0.3928 (5)	0.4956 (3)	0.1686 (3)	0.0354 (11)
C(4'B)	0.3304 (6)	0.3340 (5)	0.1172 (4)	0.031 (2)
O(4'B)	0.2207 (4)	0.3489 (3)	0.0663 (3)	0.0303 (11)
C(5'B)	0.3309 (7)	0.2293 (5)	0.1443 (5)	0.039 (2)
O(5'B)	0.2289 (5)	0.2070 (4)	0.1971 (3)	0.0427 (13)

Table 4. Selected geometric parameters (Å, °) for (2)

C(1A)—N(1A)	1.476 (9)	N(1B)—C(2B)	1.363 (9)
N(1A)—C(2A)	1.359 (9)	N(1B)—C(6B)	1.419 (9)
N(1A)—C(6A)	1.415 (9)	N(1B)—C(1B)	1.465 (8)
C(2A)—N(3A)	1.313 (8)	C(2B)—N(3B)	1.301 (9)
N(3A)—C(4A)	1.368 (8)	N(3B)—C(4B)	1.369 (9)
C(4A)—C(5A)	1.373 (9)	C(4B)—N(9B)	1.371 (9)
C(4A)—N(9A)	1.366 (8)	C(4B)—C(5B)	1.368 (9)
C(5A)—N(7A)	1.383 (9)	C(5B)—N(7B)	1.387 (9)
C(5A)—C(6A)	1.453 (10)	C(5B)—C(6B)	1.419 (10)
N(7A)—C(8A)	1.308 (9)	N(7B)—C(8B)	1.313 (9)
C(8A)—N(9A)	1.381 (8)	C(8B)—N(9B)	1.381 (9)
N(9A)—C(1'A)	1.445 (8)	N(9B)—C(1'B)	1.455 (8)
C(1'A)—O(4'A)	1.414 (8)	C(1'B)—O(4'B)	1.419 (8)
C(1'A)—C(2'A)	1.519 (9)	C(1'B)—C(2'B)	1.514 (9)
C(2'A)—C(3'A)	1.533 (10)	C(2'B)—C(3'B)	1.528 (9)
C(3'A)—C(4'A)	1.525 (10)	C(3'B)—C(4'B)	1.527 (9)
C(4'A)—O(4'A)	1.461 (8)	C(4'B)—O(4'B)	1.452 (8)
C(4'A)—C(5'A)	1.520 (10)	C(4'B)—C(5'B)	1.500 (9)
C(2A)—N(1A)—C(6A)	124.6 (6)	C(2B)—N(1B)—C(6B)	122.9 (6)
C(2A)—N(1A)—C(1A)	118.4 (6)	C(2B)—N(1B)—C(1B)	119.2 (6)
C(6A)—N(1A)—C(1A)	116.9 (6)	C(6B)—N(1B)—C(1B)	117.7 (6)
O(4'A)—C(1'A)—N(9A)	108.7 (5)	O(4'B)—C(1'B)—N(9B)	107.1 (5)
O(4'A)—C(1'A)—C(2'A)	106.1 (5)	O(4'B)—C(1'B)—C(2'B)	105.7 (5)
N(9A)—C(1'A)—C(2'A)	115.1 (6)	N(9B)—C(1'B)—C(2'B)	113.6 (5)

For both compounds, program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1267). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-(±)-2-(4-Methoxyphenyl)-4-oxo-2,3,4,5-tetrahydro-1,5-benzothiazepin-3-yl Acetate

P. KUMARADHAS AND K. A. NIRMALA

Department of Physics, Bangalore University, Bangalore 560 056, India

K. RAVIKUMAR

Laboratory of Crystallography, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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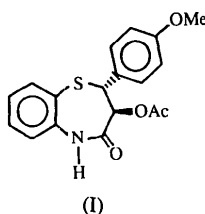
Abstract

The title compound, C₁₈H₁₇NO₄S, is a diltiazem-related compound. The molecular packing is predominantly stabilized by hydrogen bonding; amide groups hydrogen bond with adjacent molecules to form centrosymmetric dimers. The seven-membered ring is distorted, showing a twist-boat conformation. The benzene ring is planar but the methoxyphenyl ring deviates significantly from planarity. The relative configuration of the methoxyphenyl and acetoxy groups is *gauche*.

Comment

The title compound, (I), is a drug intermediate in the synthesis of diltiazem, (II), an enantiomerically pure

drug with calcium antagonist activity (Kojic Prodic, Ruzic Toros & Sunjic, 1984). The pharmacological action of (I) is not yet confirmed, but enantiomeric compounds of (I) behave as chiral solvating agents (Giordano & Restelli, 1991). The structure of compound (I) is very similar to that of diltiazem and has been compared with that of 1,4-benzothiazepine, (III) (Thomas, Paul, Williams, Grethe & Uskokovic, 1969). Interatomic distances and angles in the 1,5-benzothiazepine ring reflect usual seven-membered ring geometry and hybridization of atoms. The bond lengths S—C(1) [1.766 (3) Å] and C(9)—S [1.837 (3) Å] are unequal as one is affected by the conjugation of the adjacent π -electron system. Bond lengths involving C_{sp^3} atoms range from 1.501 (3) to 1.533 (4) Å. The carbonyl bonds fall into three categories: C_{sp^3} —O single bonds [C(8)—O(2) 1.436 (3) and C(16)—O(4) 1.411 (5) Å], C_{sp^2} —O single bonds [C(13)—O(4) 1.372 (3) and C(17)—O(2) 1.336 (3) Å] and C=O double bonds [C(17)=O(1) 1.197 (4) and C(7)=O(3) 1.239 (3) Å]. The C—N distances are unequal [C(6)—N 1.427 (3) and C(7)—N 1.341 (3) Å] as a result of different environments.



The conformation of the benzothiazepine ring is determined by considering the mean-plane deviations: S and N lie 0.490 and 0.619 Å, respectively, above the mean plane of C(7) [−0.031 Å] and C(9) [−0.011 Å], with C(6), C(8) and C(1) lying 0.268, 0.341 and 0.456 Å, respectively, below the mean plane. The values of the torsion angles of the benzothiazepine ring reflect a twist-boat conformation (Hendrickson, 1961). Acetoxy

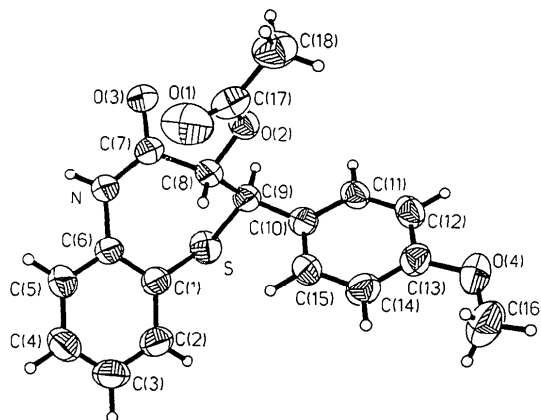


Fig. 1. A perspective view of the title molecule with the atom labelling. Displacement ellipsoids are shown at 50% probability; H atoms are represented by spheres of arbitrary radii.

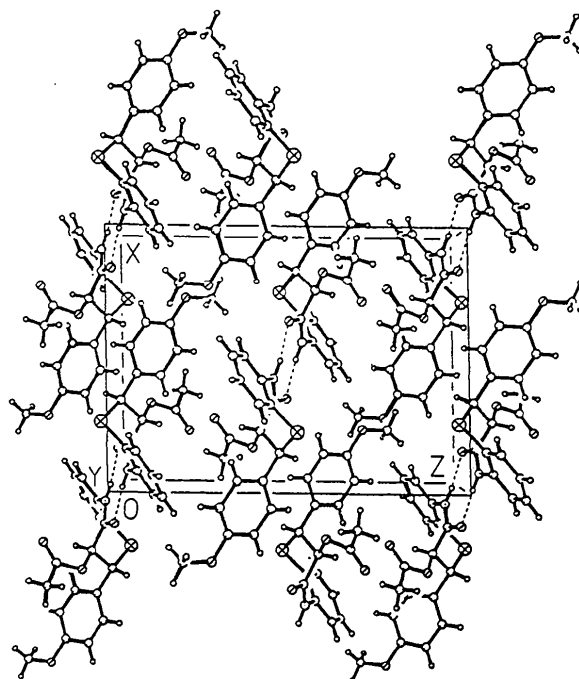


Fig. 2. Packing diagram viewed along the *b* axis.

and methoxyphenyl groups at C(8) and C(9) are *gauche* oriented as the torsion angle O(2)—C(8)—C(9)—C(10) is 61.54 (3)°.

The molecular packing is predominantly stabilized by hydrogen bonds involving the amide groups of adjacent molecules, thus forming centrosymmetric dimers in the crystal. The N—H(N)···O(3ⁱ) distance is 2.882 Å, N—H(N) and H(N)···O(3ⁱ) are 0.906 and 1.986 Å, respectively; the angles C(7)—N···O(3ⁱ) and C(6)—N···O(3ⁱ) and C(7)—O(3)···Nⁱ are 120, 118.2 and 121.9°, respectively [symmetry code: (i) $-x, 1-y, -z$]. These dimensions are fully consistent with N—H···O hydrogen bonding (Pimentel & McClellan, 1960).

Experimental

(2*R*,3*S*)-3-(4-Methoxyphenyl)methylglycidate was treated with 2-aminothiophenol in the presence of triethylamine. The resulting product was hydrolysed and treated with acetic anhydride and pyridine to obtain compound (I). Recrystallization was from ethanol. The crystal density D_m was measured by flotation in xylene—CCl₄.

Crystal data

C₁₈H₁₇NO₄S
 $M_r = 343.4$
 Monoclinic
 $P2_1/n$
 $a = 11.984 (2) \text{ \AA}$
 $b = 8.769 (1) \text{ \AA}$
 $c = 16.215 (2) \text{ \AA}$
 $\beta = 91.24 (2)^\circ$

Mo $K\alpha$ radiation
 $\lambda = 0.7107 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 7-18^\circ$
 $\mu = 0.21 \text{ mm}^{-1}$
 $T = 294 \text{ K}$
 Needle

$V = 1703.6(1) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.339 \text{ Mg m}^{-3}$
 $D_m = 1.328 \text{ Mg m}^{-3}$

Data collection

Siemens R3m/V diffractometer

$\omega/2\theta$ scans

Absorption correction:
none

2554 measured reflections

1229 independent reflections

1816 observed reflections
 $[I > 4\sigma(I)]$

$0.18 \times 0.17 \times 0.15 \text{ mm}$
Colourless

$R_{\text{int}} = 0.09$

$\theta_{\text{max}} = 22.5^\circ$

$h = 0 \rightarrow 12$

$k = 0 \rightarrow 9$
 $l = -17 \rightarrow 17$

2 standard reflections

monitored every 98

reflections
intensity decay: < 1%

Refinement

Refinement on F

$R = 0.039$

$wR = 0.048$

$S = 0.91$

1816 reflections

217 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0047F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$

Atomic scattering factors

from *SHELXTL-Plus*

(Sheldrick, 1990)

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S	0.7389 (1)	0.1226 (1)	0.0232 (1)	0.060 (1)
O(1)	0.7799 (2)	0.5466 (3)	-0.2080 (2)	0.092 (1)
O(2)	0.6713 (2)	0.5067 (2)	-0.1014 (1)	0.048 (1)
O(3)	0.8544 (2)	0.5493 (2)	-0.0053 (1)	0.063 (1)
O(4)	0.2675 (2)	0.1487 (3)	-0.2132 (2)	0.077 (1)
N	0.9311 (2)	0.3247 (3)	-0.0412 (1)	0.056 (1)
C(1)	0.8402 (2)	0.0730 (3)	-0.0496 (2)	0.050 (1)
C(2)	0.8433 (3)	-0.0772 (3)	-0.0784 (2)	0.062 (1)
C(3)	0.9294 (3)	-0.1270 (3)	-0.1266 (2)	0.070 (1)
C(4)	1.0139 (3)	-0.0290 (3)	-0.1467 (2)	0.064 (1)
C(5)	1.0136 (2)	0.1205 (3)	-0.1193 (2)	0.057 (1)
C(6)	0.9266 (2)	0.1719 (3)	-0.0713 (2)	0.050 (1)
C(7)	0.8450 (2)	0.4219 (3)	-0.0378 (2)	0.049 (1)
C(8)	0.7361 (2)	0.3743 (3)	-0.0799 (2)	0.045 (1)
C(9)	0.6596 (2)	0.2787 (3)	-0.0257 (2)	0.046 (1)
C(10)	0.5560 (2)	0.2320 (3)	-0.0728 (1)	0.044 (1)
C(11)	0.4522 (2)	0.2906 (3)	-0.0521 (2)	0.047 (1)
C(12)	0.3587 (2)	0.2594 (3)	-0.0991 (2)	0.055 (1)
C(13)	0.3654 (2)	0.1684 (3)	-0.1689 (2)	0.054 (1)
C(14)	0.4664 (3)	0.1071 (3)	-0.1895 (2)	0.057 (1)
C(15)	0.5606 (2)	0.1382 (3)	-0.1416 (2)	0.055 (1)
C(16)	0.2712 (3)	0.0637 (5)	-0.2870 (2)	0.096 (2)
C(17)	0.7006 (3)	0.5831 (3)	-0.1688 (2)	0.057 (1)
C(18)	0.6239 (3)	0.7123 (3)	-0.1866 (2)	0.075 (1)

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

S—C(1)	1.766 (3)	C(3)—C(4)	1.373 (5)
S—C(9)	1.837 (3)	C(4)—C(5)	1.384 (4)
O(1)—C(17)	1.197 (4)	C(5)—C(6)	1.391 (4)
O(2)—C(8)	1.436 (3)	C(7)—C(8)	1.519 (4)
O(2)—C(17)	1.336 (3)	C(9)—C(8)	1.533 (4)
O(3)—C(7)	1.239 (3)	C(9)—C(10)	1.501 (3)
O(4)—C(13)	1.372 (3)	C(10)—C(11)	1.393 (4)
O(4)—C(16)	1.411 (5)	C(10)—C(15)	1.389 (4)
N—C(6)	1.427 (3)	C(11)—C(12)	1.369 (4)
N—C(7)	1.341 (3)	C(12)—C(13)	1.389 (4)
C(1)—C(2)	1.398 (4)	C(13)—C(14)	1.373 (4)
C(1)—C(6)	1.401 (4)	C(14)—C(15)	1.384 (4)
C(2)—C(3)	1.379 (5)	C(17)—C(18)	1.484 (4)

C(1)—S—C(9)	104.6 (1)	C(7)—C(8)—C(9)	114.2 (2)
C(8)—O(2)—C(17)	116.9 (2)	S—C(9)—C(8)	110.2 (2)
C(13)—O(4)—C(16)	117.9 (3)	S—C(9)—C(10)	115.5 (2)
C(6)—N—C(7)	126.0 (2)	C(8)—C(9)—C(10)	110.8 (2)
S—C(1)—C(2)	118.6 (2)	C(9)—C(10)—C(11)	120.7 (2)
S—C(1)—C(6)	122.5 (2)	C(9)—C(10)—C(15)	121.6 (2)
C(2)—C(1)—C(6)	118.3 (3)	C(11)—C(10)—C(15)	117.6 (2)
C(1)—C(2)—C(3)	120.9 (3)	C(10)—C(11)—C(12)	121.1 (2)
C(2)—C(3)—C(4)	120.0 (3)	C(11)—C(12)—C(13)	120.5 (3)
C(3)—C(4)—C(5)	120.7 (3)	O(4)—C(13)—C(12)	115.8 (2)
C(4)—C(5)—C(6)	119.6 (3)	O(4)—C(13)—C(14)	124.9 (3)
N—C(6)—C(1)	121.2 (2)	C(12)—C(13)—C(14)	119.4 (3)
N—C(6)—C(5)	118.2 (2)	C(13)—C(14)—C(15)	120.0 (3)
C(1)—C(6)—C(5)	120.5 (2)	C(10)—C(15)—C(14)	121.4 (3)
O(3)—C(7)—C(8)	120.6 (2)	O(1)—C(17)—O(2)	121.8 (3)
N—C(7)—C(8)	117.5 (2)	O(1)—C(17)—C(18)	126.6 (3)
O(2)—C(8)—C(7)	110.0 (2)	O(2)—C(17)—C(18)	111.7 (3)
O(2)—C(8)—C(9)	104.7 (2)		
S—C(9)—C(8)—C(7)		-48.9 (2)	
C(9)—C(8)—C(7)—N		86.9 (3)	
C(8)—C(7)—N—C(6)		-8.8 (4)	
C(7)—N—C(6)—C(1)		-44.3 (4)	
N—C(6)—C(1)—S		-6.1 (4)	
C(6)—C(1)—S—C(9)		66.4 (3)	
C(1)—S—C(9)—C(8)		-32.8 (2)	
S—C(9)—C(10)—C(15)		-62.9 (3)	
S—C(9)—C(8)—O(2)		-169.3 (1)	
C(9)—C(8)—O(2)—C(17)		-158.0 (2)	
C(8)—O(2)—C(17)—C(18)		177.1 (2)	
C(8)—O(2)—C(17)—O(1)		-2.7 (4)	
O(2)—C(8)—C(9)—C(10)		61.5 (3)	

H atoms were located from difference Fourier maps; they were positioned geometrically and included as riding atoms with fixed isotropic displacement parameters in the structure-factor calculations.

Cell refinement: Siemens R3m/V software. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1102). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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