

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1150). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Methyl-4*H*-pyrido[4,3-*e*][1,2,4]thiadiazine 1,1-Dioxide Monohydrate

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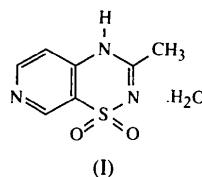
Abstract

The title compound, C₇H₇N₃O₂S.H₂O, was prepared for structural and pharmacological comparison with diazoxide, an antihypertensive agent. The crystal structure determination shows that the 4*H* (rather than 2*H*) tautomeric form is preferentially adopted by this pyridothiadiazine derivative in the solid state.

Comment

Little has been reported on the pyrido[4,3-*e*][1,2,4]-thiadiazine 1,1-dioxide ring system. Only a few 4-aryl- and 3-aminoalkyl-4*H*-pyrido[4,3-*e*][1,2,4]thiadiazine 1,1-dioxides have been described (Delarge & Lapière,

1974; Pirotte, de Tullio, Lebrun, Antoine, Fontaine, Masereel, Schynts, Dupont, Herchuelz & Delarge, 1993). The title compound (I) also contains this ring system and is related structurally to diazoxide [7-chloro-3-methyl-2*H*(or 4*H*)-1,2,4-benzothiadiazine 1,1-dioxide], a well known antihypertensive agent currently reported as the pharmacological reference for the benzothiadiazine class of ATP-sensitive potassium-channel openers (Edwards & Weston, 1990).



The X-ray analysis of the title compound may help to determine whether the 2*H* or 4*H* tautomer is the preferred form in the solid state. The thiadiazine molecule is linked to the water molecule by the hydrogen bonds N4—H4···O14 [N4···O14 2.734 (3), H4···O14 1.89 (4) Å, N4—H4···O14 171 (3)°] and O14—H142···N8ⁱ [O14···N8ⁱ 2.775 (3), H142···N8ⁱ 1.76 (2) Å, O14—H142···N8ⁱ 179 (2)°; symmetry code: (i) $x - \frac{1}{2}, -\frac{1}{2} - y, \frac{1}{2} + z$]. The N2—C3 and N4—C3 bond lengths, the location of the H atom on atom N4 rather than N2 and the hydrogen-bonding scheme all indicate that the 4*H* tautomeric form is favoured in the crystal. The same conclusion has been made for diazoxide [N2—C3 1.300 (9) and N4—C3 1.335 (9) Å; Bandoli & Nicolini, 1977] and the [3,2-*e*] derivative [N2—C3 1.306 (7) and N4—C3 1.328 (6) Å; Dupont, Pirotte, de Tullio, Masereel & Delarge, 1995].

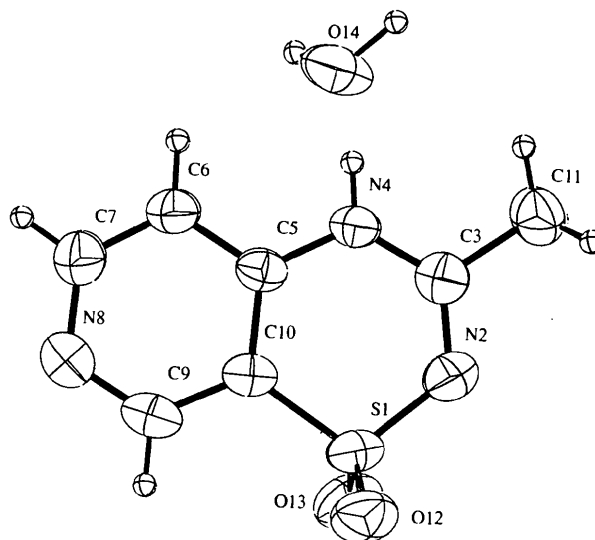


Fig. 1. The molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

Experimental

Crystal data

C₇H₇N₃O₂S.H₂OM_r = 215.23

Monoclinic

P2₁/n

a = 9.3055 (6) Å

b = 8.4118 (6) Å

c = 12.3965 (7) Å

β = 98.731 (7)°

V = 959.10 (11) Å³

Z = 4

D_x = 1.491 Mg m⁻³

Cu Kα radiation

λ = 1.54180 Å

Cell parameters from 52 reflections

θ = 18.72–37.15°

μ = 2.934 mm⁻¹

T = 293 (2) K

Prism

0.53 × 0.42 × 0.34 mm

Colourless

Crystal source: Laboratory of Medicinal Chemistry, Liège

Data collection

Stoe–Siemens AED four-circle diffractometer

ω scans

Absorption correction: semi-empirical via ψ scans

T_{min} = 0.3486, T_{max} = 0.4475

1202 measured reflections

1202 independent reflections

1119 observed reflections [I > 2σ(I)]

θ_{max} = 55.01°

h = 0 → 9

k = 0 → 8

l = -13 → 12

2 standard reflections

frequency: 60 min intensity decay: 2.5%

Refinement

Refinement on F²

R(F) = 0.0375

wR(F²) = 0.1020

S = 1.089

1202 reflections

134 parameters

w = 1/[σ²(F_o²) + (0.0618P)² + 0.4223P]where P = (F_o² + 2F_c²)/3(Δ/σ)_{max} < 0.001Δρ_{max} = 0.23 e Å⁻³Δρ_{min} = -0.34 e Å⁻³

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.086 (4)

Atomic scattering factors

from *International Tables for Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 2. Selected geometric parameters (Å, °)

S1—O12	1.425 (2)	N4—C5	1.376 (3)
S1—O13	1.430 (2)	C5—C6	1.388 (3)
S1—N2	1.603 (3)	C5—C10	1.393 (3)
S1—C10	1.737 (2)	C6—C7	1.364 (4)
N2—C3	1.305 (4)	C7—N8	1.344 (4)
C3—N4	1.335 (3)	N8—C9	1.321 (3)
C3—C11	1.501 (4)	C9—C10	1.386 (4)
O12—S1—O13	115.35 (13)	N4—C5—C6	121.5 (2)
O12—S1—N2	108.77 (13)	N4—C5—C10	120.9 (2)
O13—S1—N2	109.36 (14)	C6—C5—C10	117.6 (2)
O12—S1—C10	109.13 (12)	C7—C6—C5	119.1 (2)
O13—S1—C10	108.38 (12)	N8—C7—C6	124.1 (3)
N2—S1—C10	105.39 (11)	C9—N8—C7	116.6 (2)
C3—N2—S1	123.8 (2)	N8—C9—C10	123.9 (2)
N2—C3—N4	125.4 (2)	C9—C10—C5	118.7 (2)
N2—C3—C11	118.6 (2)	C9—C10—S1	121.6 (2)
N4—C3—C11	116.0 (2)	C5—C10—S1	119.7 (2)
C3—N4—C5	124.6 (2)		
O12—S1—N2—C3	-121.0 (3)	C11—C3—N4—C5	-177.3 (2)
O13—S1—N2—C3	112.2 (3)	C3—N4—C5—C10	-3.8 (4)
C10—S1—N2—C3	-4.1 (3)	N4—C5—C10—S1	0.7 (3)
S1—N2—C3—N4	2.0 (4)	O12—S1—C10—C5	119.4 (2)
S1—N2—C3—C11	-178.2 (2)	O13—S1—C10—C5	-114.2 (2)
N2—C3—N4—C5	2.6 (4)	N2—S1—C10—C5	2.7 (2)

During refinement, riding H atoms were included at calculated positions except for atom H4(N4), which was freely refined, and the water H atoms, whose positions were obtained from a Fourier difference map and subsequently kept fixed.

Data collection: *DIF4* (Stoe & Cie, 1987a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1987b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including bond distances and angles involving H atoms, and torsion angles have been deposited with the IUCr (Reference: MU1153). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
S1	0.83365 (6)	0.02798 (8)	0.13155 (5)	0.0508 (4)
N2	0.7520 (3)	0.0549 (3)	0.2350 (2)	0.0618 (7)
C3	0.6257 (3)	-0.0067 (3)	0.2441 (2)	0.0485 (7)
N4	0.5489 (2)	-0.1031 (3)	0.1715 (2)	0.0448 (6)
C5	0.5946 (2)	-0.1568 (3)	0.0775 (2)	0.0405 (6)
C6	0.5122 (3)	-0.2632 (3)	0.0083 (2)	0.0507 (7)
C7	0.5616 (3)	-0.3108 (3)	-0.0846 (2)	0.0580 (8)
N8	0.6869 (3)	-0.2610 (3)	-0.1148 (2)	0.0614 (7)
C9	0.7656 (3)	-0.1607 (3)	-0.0483 (2)	0.0572 (8)
C10	0.7254 (2)	-0.1049 (3)	0.0480 (2)	0.0435 (7)
C11	0.5587 (4)	0.0318 (3)	0.3438 (2)	0.0636 (8)
O12	0.9714 (2)	-0.0436 (3)	0.1676 (2)	0.0671 (6)
O13	0.8381 (2)	0.1747 (2)	0.0739 (2)	0.0737 (7)
O14	0.2734 (2)	-0.2085 (3)	0.1817 (2)	0.0781 (8)

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trans-2-[(Dispiro[2.0.2.1]hept-7-yl)-carbonyl]-3-methyl- β -propiolactone

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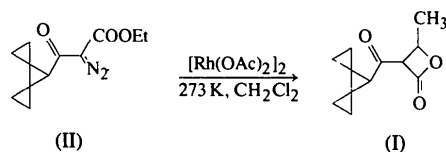
Abstract

The title compound, C₁₂H₁₄O₃, has a *trans* configuration of substituents in the β -lactone ring and an *exo* orientation of the carbonyl group with respect to the dispiroheptane moiety. The presence of a π -accepting carbonyl group causes elongation of the vicinal bonds and contraction of the distal one in the central three-membered ring. The difference in vicinal bond lengths is possibly a result of an asymmetric orientation of the carbonyl group.

Comment

The present work is part of our structural study of a relatively new class of hydrocarbons, *i.e.* polyspirocyclopropanes (triangulanes; Zefirov *et al.*, 1990) and their derivatives. Standard bond lengths for different kinds of bond in the triangulanes were calculated and found to be predictable on the basis of a simple scheme of substituent-effect addition (Lukin, Kozhushkov, Zefirov, Yufit & Struchkov, 1993). A similar conclusion was reached previously on the basis of a detailed study of the derivatives of the smallest triangulane, *i.e.* spiropentane (Irgartinger, Grieg, Klans & Gleiter, 1992). Recently, we have published (Yufit, Antipin, Lukin, Struchkov & Zefirov, 1993) the results of a charge-density study of dispiro[2.0.2.1]heptane-1-carboxylic acid, the first triangulane with a π -acceptor substituent, and discussed the

effect of the carboxy group on the molecular geometry. For a comparison of the effect of carbonyl-containing substituents in the 1- and 7-positions on the geometrical parameters of the dispiro[2.0.2.1]heptane skeleton, the X-ray crystallographic study of the title compound (I) was performed. The compound is a product of an unexpected intramolecular cyclization of (II), and its configuration was unknown.



Atoms C(8) and C(12) are located on opposite sides of the four-membered β -lactone ring plane (planar within 0.015 Å), which means that (I) has a *trans* configuration. The antiperiplanar (*ap*) orientation of the carbonyl group on the triangulane moiety is rather uncommon for triangulane, as well as for cyclopropane derivatives where the carbonyl group prefers the synperiplanar orientation (Allen, 1980). The bond lengths in the terminal three-membered rings are in good agreement with standard values (1.528 Å for terminal and 1.480 Å for central bonds). As in the previously studied triangulanes, the effect of the π -accepting carbonyl group is seen in contraction of the distal C(3)—C(4) bond and elongation of the vicinal C(3)—C(7) and C(4)—C(7) bonds. Using the standard values for bond lengths in triangulanes and Allen's (Allen, 1980) distal bond-lengthening parameter ($\delta_{\bar{C}=\text{O}} = 0.026$ Å), one can calculate the expected interatomic distances in the central ring of (I); 1.437 Å for the distal bond and 1.513 Å for the vicinal bonds. The observed values for the C(3)—C(4) and C(7)—C(4) bond lengths correspond well with those calculated, but the C(3)—C(7) distance of 1.530 (2) Å is elongated. There are no close intramolecular non-bonded contacts with C(3) and the

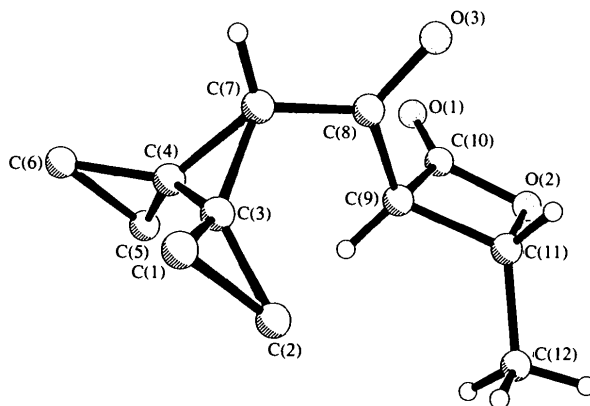


Fig. 1. The geometry and atom-labelling scheme of molecule (I) (H atoms of the triangulane CH₂ groups are omitted for clarity).

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