

C3—N2—C11	114.5 (9)	C9—N8—C13	121.2 (9)
C3—N2—S1	110.6 (7)	C7—N8—C13	120.4 (9)
C11—N2—S1	116.7 (8)	N8—C9—C10	121.4 (9)
N2—C3—N4	111.4 (9)	C9—C10—C5	121.6 (9)
C5—N4—C3	121.8 (8)	C9—C10—S1	119.0 (8)
C5—N4—C12	121.7 (9)	C5—C10—S1	119.3 (8)
C3—N4—C12	116.1 (9)		
O1—S1—N2—C3	-57.9 (8)	C12—N4—C5—C10	-177.9 (9)
O2—S1—N2—C3	171.4 (7)	N4—C5—C6—C7	176.3 (10)
C10—S1—N2—C3	56.1 (8)	C6—C7—N8—C13	-176.9 (11)
O1—S1—N2—C11	168.8 (8)	C13—N8—C9—C10	178.0 (11)
O2—S1—N2—C11	38.1 (9)	N4—C5—C10—C9	-175.3 (10)
C10—S1—N2—C11	-77.2 (9)	N4—C5—C10—S1	1.2 (13)
C11—N2—C3—N4	67.4 (12)	O1—S1—C10—C9	-94.9 (9)
S1—N2—C3—N4	-67.0 (10)	O2—S1—C10—C9	36.5 (10)
N2—C3—N4—C5	39.0 (14)	N2—S1—C10—C9	151.3 (8)
N2—C3—N4—C12	-148.3 (10)	O1—S1—C10—C5	88.5 (9)
C3—N4—C5—C6	176.6 (10)	O2—S1—C10—C5	-140.0 (8)
C12—N4—C5—C6	4.3 (15)	N2—S1—C10—C5	-25.2 (9)
C3—N4—C5—C10	-5.6 (14)		

Data collection: *DIF4* (Stoe & Cie, 1987a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1987c). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

The authors thank M. M. Vermeire for his helpful assistance in the diffractometry measurements and the Belgian FNRS (Fonds National de la Recherche Scientifique) for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: PA1187). 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**, 2414–2416

3,7-Dimethyl-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-Dioxide Zwitterion

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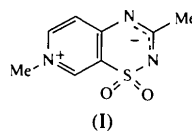
(Received 4 May 1995; accepted 19 June 1995)

Abstract

The title compound, 3,7-dimethyl-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazin-7-ium-2/4-ide 1,1-dioxide, C₈H₉N₃O₂S, is the 7-methyl derivative of a product previously described as a structural analogue of the antihypertensive agent diazoxide. This novel structure is an unusual pyridinium-containing heterocycle isolated from water at neutral pH as a zwitterionic species, the corresponding 4*H*-protonated species exhibiting strong acidic character. The crystal structure determination shows a delocalization of the negative charge between the N atoms at the 2 and 4 positions.

Comment

The title compound, (I), is a derivative of 3-methyl-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-dioxide (de Tullio *et al.*, 1995). These compounds are structurally related to diazoxide [7-chloro-3-methyl-2*H*(or 4*H*)-1,2,4-benzothiadiazine 1,1-dioxide], a well known antihypertensive drug (Bandoli & Nicolini, 1977).



The C7—N8—C9 angle [120.0(3)°] is typical for a pyridinium ring (Dupont, Pirotte, de Tullio, Diouf, Masereel & Delarge, 1995). The values of the torsion angles show that the molecule is almost planar. N4, S1 and C12 deviate from the pyridinium mean plane by -0.102(5), 0.125(4) and -0.027(6) Å, respectively. The molecule is a zwitterion with a negative charge delocalized in the crystal between N2 and N4. The N2—C3 [1.335(4) Å] and C3—N4 [1.332(4) Å] bond

lengths are intermediate between those of single and double bonds. In the 3-methyl derivative (de Tullio *et al.*, 1995), the corresponding values are 1.299 (3) for N2—C3 (a double bond) and 1.364 (3) Å for C3—N4 (a single bond). There are no hydrogen bonds.

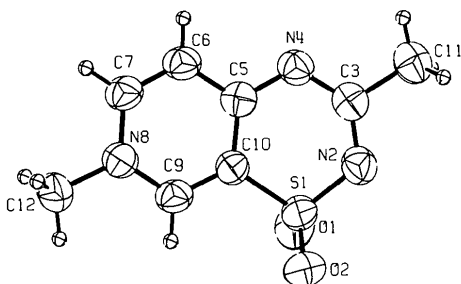


Fig 1. Molecular structure with atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

Experimental

The title compound was synthesized at the Laboratory of Medicinal Chemistry of Liège. The method will be published elsewhere. Crystals were obtained by slow evaporation of a water–methanol solution (75/25% by volume) at room temperature.

Crystal data

$C_8H_9N_3O_2S$
 $M_r = 211.24$
 Monoclinic
 $P2_1/a$
 $a = 12.641(2) \text{ \AA}$
 $b = 5.5304(10) \text{ \AA}$
 $c = 13.615(3) \text{ \AA}$
 $\beta = 105.847(15)^\circ$
 $V = 915.7(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.532 \text{ Mg m}^{-3}$

Data collection

Stoe Siemens AED four-circle diffractometer
 ω scans
 Absorption correction: ψ scan (EMPIR; Stoe & Cie, 1987b)
 $T_{\min} = 0.526$, $T_{\max} = 0.694$
 1234 measured reflections
 1234 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0454$
 $wR(F^2) = 0.1208$
 $S = 1.063$
 1234 reflections

Cu $K\alpha$ radiation
 $\lambda = 1.5418 \text{ \AA}$
 Cell parameters from 29 reflections
 $\theta = 27.39\text{--}32.65^\circ$
 $\mu = 2.980 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Prism
 $0.30 \times 0.15 \times 0.12 \text{ mm}$
 Colourless

907 observed reflections
 $[I > 2\sigma(I)]$
 $\theta_{\max} = 57.52^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 6$
 $l = -14 \rightarrow 14$
 2 standard reflections
 frequency: 60 min
 intensity decay: 2.5%

$\Delta\rho_{\max} = 0.223 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.242 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL93 (Sheldrick, 1993)

130 parameters
 H atoms were restrained (included as riding atoms)
 $w = 1/[\sigma^2(F_o^2) + (0.0953P)^2 + 0.2229P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.005$

Extinction coefficient: 0.0385 (29)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
S1	0.76031 (6)	0.1487 (2)	0.80610 (6)	0.0599 (4)
N2	0.7336 (2)	-0.0222 (5)	0.7088 (2)	0.0638 (8)
C3	0.6711 (3)	0.0570 (6)	0.6190 (3)	0.0577 (9)
N4	0.6062 (2)	0.2506 (6)	0.5979 (2)	0.0599 (8)
C5	0.5922 (3)	0.3861 (6)	0.6767 (2)	0.0548 (8)
C6	0.5113 (3)	0.5687 (6)	0.6578 (2)	0.0586 (9)
C7	0.4901 (2)	0.6948 (6)	0.7350 (2)	0.0582 (9)
N8	0.5482 (2)	0.6523 (5)	0.8343 (2)	0.0566 (7)
C9	0.6275 (3)	0.4855 (6)	0.8555 (2)	0.0568 (9)
C10	0.6516 (2)	0.3536 (6)	0.7801 (2)	0.0527 (8)
C11	0.6700 (3)	-0.1057 (7)	0.5303 (3)	0.0706 (10)
C12	0.5220 (3)	0.7935 (8)	0.9172 (3)	0.0713 (11)
O1	0.8607 (2)	0.2804 (5)	0.8140 (2)	0.0800 (8)
O2	0.7589 (2)	0.0090 (5)	0.8955 (2)	0.0776 (8)

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

S1—O1	1.442 (3)	C5—C6	1.410 (5)
S1—O2	1.445 (3)	C5—C10	1.414 (5)
S1—N2	1.587 (3)	C6—C7	1.348 (4)
S1—C10	1.741 (3)	C7—N8	1.371 (4)
N2—C3	1.335 (4)	N8—C9	1.334 (4)
C3—N4	1.332 (4)	N8—C12	1.481 (4)
C3—C11	1.504 (4)	C9—C10	1.360 (4)
N4—C5	1.360 (4)		
O1—S1—O2	114.9 (2)	N4—C5—C10	124.6 (3)
O1—S1—N2	110.2 (2)	C6—C5—C10	115.8 (3)
O2—S1—N2	109.6 (2)	C7—C6—C5	121.1 (3)
O1—S1—C10	108.4 (2)	C6—C7—N8	120.9 (3)
O2—S1—C10	109.18 (15)	C9—N8—C7	120.0 (3)
N2—S1—C10	103.99 (15)	C9—N8—C12	120.7 (3)
C3—N2—S1	120.4 (2)	C7—N8—C12	119.3 (3)
N4—C3—N2	129.6 (3)	N8—C9—C10	121.2 (3)
N4—C3—C11	115.9 (3)	C9—C10—C5	121.0 (3)
N2—C3—C11	114.3 (3)	C9—C10—S1	121.5 (2)
C3—N4—C5	118.5 (3)	C5—C10—S1	117.4 (2)
N4—C5—C6	119.7 (3)		
O1—S1—N2—C3	-91.2 (3)	C6—C7—N8—C12	-179.6 (3)
O2—S1—N2—C3	141.5 (3)	N8—C9—C10—S1	176.1 (2)
C10—S1—N2—C3	24.8 (3)	N4—C5—C10—S1	7.4 (4)
S1—N2—C3—N4	-14.4 (5)	C6—C5—C10—S1	-174.6 (2)
S1—N2—C3—C11	169.2 (2)	N2—S1—C10—C9	161.1 (3)
N2—C3—N4—C5	-5.1 (5)	O1—S1—C10—C5	95.6 (3)
C11—C3—N4—C5	171.3 (3)	O2—S1—C10—C5	-138.6 (3)
C3—N4—C5—C6	-170.1 (3)	N2—S1—C10—C5	-21.7 (3)
C3—N4—C5—C10	7.8 (5)		

Data collection: DIF4 (Stoe & Cie, 1987a). Cell refinement: DIF4. Data reduction: REDU4 (Stoe & Cie, 1987c). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). 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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Acta Cryst. (1995). **C51**, 2416–2417

7-Methyl-3-methylthio-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazin-7-ium-4-ide 1,1-Dioxide Zwitterion

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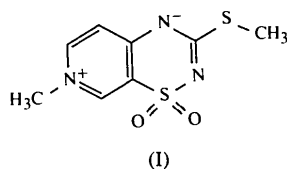
Abstract

The title compound, C₈H₉N₃O₂S₂, is an original drug structurally related to diazoxide, an antihypertensive compound. At neutral pH, the molecule is a zwitterion which contains a pyridinium heterocycle. The negative charge is localized at the 4 position.

Comment

The title compound, 7-methyl-3-methylthio-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazin-7-ium-4-ide 1,1-dioxide, (I), re-

sults from the reaction of 3-methylthio-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-dioxide with iodomethane in aqueous alkaline solution. At neutral pH, the compound is isolated as a zwitterion and is used for the synthesis of 3-aminoalkyl derivatives that have been tested as original pyridothiadiazine potassium channel openers. It is structurally related to diazoxide [7-chloro-3-methyl-2*H*(or 4*H*)-1,2,4-benzothiadiazine 1,1-dioxide], a well known antihypertensive drug (Bandoli & Nicolini, 1977).



The value of the C7—N8—C9 angle [119.2(3)°] is typical of a pyridinium ring (Dupont, Pirotte, de Tullio, Masereel & Delarge, 1995). The values of the torsion angles show that the molecule is almost planar. The deviations of atoms N4, S1 and C12 from the mean plane of the pyridinium ring are 0.032(4), −0.068(4) and 0.059(5) Å, respectively. These values are comparable with those found in the structure of the 3,7-dimethyl-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-dioxide zwitterion (Dupont *et al.*, 1995). The molecule is a zwitterion where the negative charge is localized on N4 rather than on N2. The N2—C3 bond length [1.322(4) Å] is closer to the standard double-bond value than that of the 3,7-dimethyl derivative [1.335(4) Å].

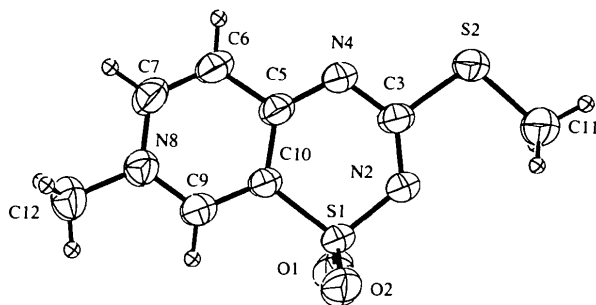


Fig. 1. The molecular structure of the title compound with the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

Experimental

The title compound was synthesized at the Laboratory of Medicinal Chemistry of Liège. The method of preparation will be published elsewhere. Crystals were obtained by slow evaporation of a water–methanol solution (75/25% by volume) at room temperature.