C(4′)—O(4′)—C(1′)—C(2′)	−38.1 (1)
C(1′)—O(4′)—C(4′)—C(3′)	17.8 (1)
C(4′A)—O(4′A)—C(1′A)—C(2′A)	−32.4 (1)
C(1′A)—O(4′A)—C(4′A)—C(3′A)	10.4 (1)
N(6′)—N(5′)—C(5′)—C(4′)	91.6 (2)
C(2)—N(1)—C(1′)—O(4′)	−142.6 (1)
C(2)—N(1)—C(1′)—C(2′)	101.6 (2)
C(6)—N(1)—C(1′)—O(4′)	45.2 (2)
C(6)—N(1)—C(1′)—C(2′)	−70.6 (2)
N(6′A)—N(5′A)—C(5′A)—C(4′A)	−162.1 (2)
C(2A)—N(1A)—C(1′A)—O(4′A)	−137.2 (1)
C(2A)—N(1A)—C(1′A)—C(2′A)	106.5 (2)
C(6A)—N(1A)—C(1′A)—O(4′A)	50.7 (2)
C(6A)—N(1A)—C(1′A)—C(2′A)	−65.6 (2)
O(4′)—C(1′)—C(2′)—C(3′)	42.9 (2)
C(1′)—C(2′)—C(3′)—C(4′)	−30.8 (2)
C(2′)—C(3′)—C(4′)—O(4′)	9.5 (2)
O(4′)—C(4′)—C(5′)—N(5′)	−65.7 (2)
C(3′)—C(4′)—C(5′)—N(5′)	54.6 (2)
O(4′A)—C(1′A)—C(2′A)—C(3′A)	41.2 (1)
C(1′A)—C(2′A)—C(3′A)—C(4′A)	−33.3 (1)
C(2′A)—C(3′A)—C(4′A)—O(4′A)	15.4 (1)
O(4′A)—C(4′A)—C(5′A)—N(5′A)	−64.6 (2)
C(3′A)—C(4′A)—C(5′A)—N(5′A)	55.6 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(3′)—H(O3′)···O(4^{i})	0.81 (2)	1.98 (3)	2.749 (2)	159 (2)
O(3′A)—H(O3′A)···O(4A^{ii})	0.90 (2)	1.92 (2)	2.751 (2)	152 (2)
N(3)—H(O3)···O(3′A^{iii})	0.88 (3)	2.05 (3)	2.905 (2)	163 (2)
N(3A)—H(O3A)···O(3′)	0.94 (3)	1.99 (3)	2.918 (2)	167 (2)

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (B. A. Frenz & Associates Inc., 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,4,7-Trimethyl-2,3-dihydro-4*H*-pyrido-[4,3-*e*]-1,2,4-thiadiazinium 1,1-Dioxide Iodide

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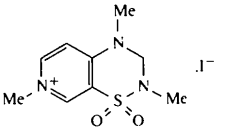
Abstract

The title compound, $C_9H_{14}N_3O_2S^+.I^-$, is a new drug developed as a structural derivative of the antihypertensive agent diazoxide. The C atom at the 3 position is sp^3 hybridized, whereas in the related compounds for which the structures have been determined so far it is sp^2 hybridized. The distances and angles around the N atom in the aromatic ring are consistent with a pyridinium cationic moiety.

Comment

The title compound, (I), is structurally related to diazide diuretics and diazoxide (Bandoli & Nicolini, 1977).



(I)

The cationic heterocycle exhibits an opening of the intra-cyclic angle C7—N8—C9 [118.3 (9)°] and a lengthening of C7—N8 and N8—C9 with respect to the values usually observed in a pyridine ring. This was also observed for 1-isopropyl-3-{[4-(1-piperidylamino)-3-pyridyl]sulfonyl}urea hydrogen nitrate (Dupont, Dideberg, Delarge, Dive & Thunus, 1982). Further examples

of the geometries of pyridine rings in thiadiazine derivatives are given by Dupont, Pirotte, de Tullio, Masereel & Delarge (1995). The pyridinium ring is planar with a maximum deviation from the mean plane of 0.013 (7) Å; the deviations of N4, S1 and C13 from this plane are −0.091 (15), −0.027 (15) and −0.070 (19) Å, respectively. The relatively high R value probably results from inaccuracies in the absorption correction, which is large due to the presence of the I atom. (All peaks with values higher than 0.49 e Å^{-3} or lower than −0.5 e Å^{-3} in the final difference map lay within the van der Waals sphere of the I atom and had no potential chemical meaning.) There are no hydrogen bonds.

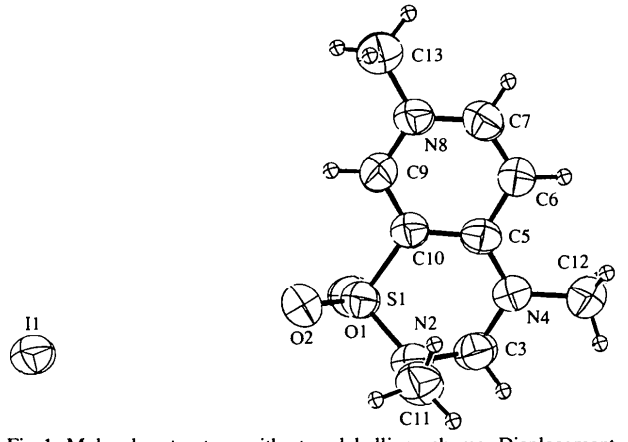


Fig 1. Molecular structure with atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

Experimental

The title compound was synthesized at the Laboratory of Medicinal Chemistry of Liège by the simultaneous methylation on the 2 and 7 positions of 4-methyl-2,3-dihydro-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-dioxide with methyl iodide in an alkaline aqueous medium. Crystals were obtained by slow evaporation of a water–methanol solution (75/25% by volume) at room temperature.

Crystal data

$C_9H_{14}N_3O_2S^+.I^-$
M_r = 355.19
Triclinic
$P\bar{1}$
a = 7.9184 (10) Å
b = 8.9446 (14) Å
c = 10.861 (2) Å
α = 109.410 (9)°
β = 107.918 (6)°
γ = 90.336 (6)°
V = 685.3 (2) Å^3
Z = 2
D_x = 1.721 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 58 reflections
θ = 23.7–35.5°
μ = 19.732 mm^{-1}
T = 293 (2) K
Prism
0.31 × 0.30 × 0.13 mm
Colourless

Data collection

Stoe Siemens AED four-circle diffractometer
ω scans
Absorption correction: ψ scan (*EMPIR*; Stoe & Cie, 1987*b*)
T_{min} = 0.081, T_{max} = 0.131
2026 measured reflections
1881 independent reflections
1703 observed reflections [$I > 2\sigma(I)$]
R_{int} = 0.0209
θ_{max} = 57.53°
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 9$
$l = -11 \rightarrow 11$
2 standard reflections
frequency: 60 min
intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0692
$wR(F^2)$ = 0.1896
S = 1.091
1877 reflections
149 parameters
H atoms were placed at standard calculated positions and restrained (included as riding atoms)
$w = 1/[\sigma^2(F_o^2) + (0.1567P)^2 + 0.9261P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 1.188 e Å^{-3}
$\Delta\rho_{min}$ = −2.836 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0087 (14)
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* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
I1	0.15578 (8)	0.30980 (8)	0.27817 (6)	0.0734 (5)
S1	−0.5279 (3)	0.7794 (3)	0.2600 (3)	0.0668 (7)
O1	−0.4445 (11)	0.9375 (10)	0.3069 (9)	0.086 (2)
O2	−0.4174 (10)	0.6530 (10)	0.2623 (9)	0.083 (2)
N2	−0.6678 (12)	0.7379 (11)	0.1039 (9)	0.069 (2)
C3	−0.8003 (16)	0.8515 (14)	0.1021 (12)	0.074 (3)
N4	−0.9180 (11)	0.8335 (10)	0.1786 (9)	0.065 (2)
C5	−0.8561 (12)	0.8039 (10)	0.2967 (10)	0.061 (2)
C6	−0.9664 (14)	0.7946 (14)	0.3749 (11)	0.073 (3)
C7	−0.9020 (15)	0.7562 (13)	0.4882 (12)	0.071 (3)
N8	−0.7319 (11)	0.7237 (10)	0.5344 (8)	0.066 (2)
C9	−0.6219 (14)	0.7333 (13)	0.4645 (11)	0.066 (2)
C10	−0.6779 (13)	0.7742 (12)	0.3498 (10)	0.062 (2)
C11	−0.7433 (16)	0.5687 (13)	0.0265 (12)	0.083 (3)
C12	−1.1023 (15)	0.8694 (15)	0.1278 (13)	0.078 (3)
C13	−0.6727 (17)	0.6744 (17)	0.6556 (14)	0.088 (3)

Table 2. *Selected geometric parameters* (Å, °)

S1—O1	1.414 (9)	N4—C12	1.472 (14)
S1—O2	1.435 (8)	C5—C6	1.412 (15)
S1—N2	1.631 (9)	C5—C10	1.414 (14)
S1—C10	1.763 (10)	C6—C7	1.34 (2)
N2—C3	1.465 (14)	C7—N8	1.355 (14)
N2—C11	1.480 (14)	N8—C9	1.339 (14)
C3—N4	1.466 (14)	N8—C13	1.468 (14)
N4—C5	1.341 (12)	C9—C10	1.359 (15)
O1—S1—O2	118.7 (5)	N4—C5—C6	122.2 (9)
O1—S1—N2	108.5 (5)	N4—C5—C10	122.7 (9)
O2—S1—N2	109.1 (5)	C6—C5—C10	115.0 (9)
O1—S1—C10	108.8 (5)	C7—C6—C5	120.4 (10)
O2—S1—C10	109.8 (5)	C6—C7—N8	123.3 (10)
N2—S1—C10	100.3 (5)	C9—N8—C7	118.3 (9)

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: *DIF*4 (Stoe & Cie, 1987*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1987*c*). 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). Software used to prepare material for publication: *SHELXL*93.

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

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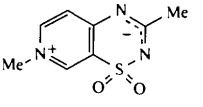
Abstract

The title compound, 3,7-dimethyl-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazin-7-ium-2/4-ide 1,1-dioxide, $C_8H_9N_3O_2S$, 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).



(I)

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