Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Amino-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-Dioxide Monohydrate and 3-*tert*-Butyl-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-Dioxide

LÉON DUPONT

Unité de Cristallographie, Institut de Physique B5, Université de Liège au Sart Tilman, B-4000 Liège, Belgium

BERNARD PIROTTE, PASCAL DE TULLIO, BERNARD MASEREEL AND JACQUES DELARGE

Laboratoire de Chimie Pharmaceutique, Institut de Pharmacie F1, Université de Liège, Rue Fusch 5, B-4000 Liège, Belgium

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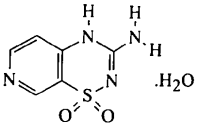
Abstract

The title compounds, $C_6H_6N_4O_2S.H_2O$, (I), and $C_{10}H_{13}N_3O_2S$, (II), were prepared for structural and pharmacological comparison with diazoxide, an antihypertensive agent. The crystal structure determinations show that the 4*H*- (rather than the 2*H*-) tautomeric form is preferentially adopted by these pyridothiadiazine derivatives in the solid state, as has also been found for diazoxide and other 1,2,4-thiadiazine 1,1-dioxide analogues. The *tert*-butyl moiety in (II) is slightly disordered.

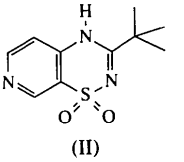
Comment

3-Amino-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-dioxide monohydrate, (I), is a heterocyclic compound for which the synthesis and the biological evaluation on insulin-secreting cells in comparison with diazoxide [7-chloro-3-methyl-2*H*(or 4*H*)-1,2,4-benzothiadiazine 1,1-dioxide] has recently been reported (Pirotte *et al.*, 1993). In the crystalline state, the thiadiazine and water molecules are linked by the hydrogen bonds N4—H4···O3 [N4···O3 2.676 (3), H4···O3 1.69 (2) Å, N4—H4···O3 165 (1)°], N11—H111···O2^{i} [N11···O2^{i} 3.100 (3), H111···O2^{i} 2.39 (2) Å, N11—H111···O2^{i} 134 (1)°], N11—H112···O1^{ii} [N11···O1^{ii} 2.959 (3), H112···O1^{ii} 2.13 (2) Å, N11—H112···O1^{ii} 162 (2)°], O3—H31···O2^{iii} [O3···O2^{iii} 2.841 (4), H31···O2^{iii} 1.87 (3) Å, O3—H31···O2^{iii} 172 (1)°] and O3—H32···N8^{iv} [O3···N8^{iv} 2.730 (3), H32···N8^{iv} 1.76 (2) Å, O3—H32···N8^{iv} 180 (1)°] [symmetry codes: (i) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $-z$; (ii) $-x$, $-y$, $-z$; (iii) $1-x$, $-y$, $-z$; (iv) $\frac{3}{2}-x$, $-\frac{1}{2}+y$, $1-z$].



(I)

3-*tert*-Butyl-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-dioxide, (II), was also investigated in order to compare its molecular structure with that of diazoxide. An article describing the preparation and the synthesis of the product, and the biological evaluation, is in preparation (Pirotte *et al.*, 1995). The molecules are linked by the hydrogen bond N4—H4···O1^{i} [N4···O1^{i} 2.981 (4), H4···O1^{i} 2.08 (2) Å, N4—H4···O1^{i} 156 (1)°; symmetry code: (i) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $1-z$].



(II)

In both crystal structures the N2—C3 and N4—C3 bond lengths, the location of the H atom on N4 rather than on N2, and the hydrogen-bonding schemes indicate that the 4*H*- form is favoured in the solid state. The same conclusion has been drawn for diazoxide

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(Bandoli & Nicolini, 1977) and for some other thiadiazine derivatives, for example 3-methyl-4*H*-pyrido-[4,3-*e*]-1,2,4-thiadiazine 1,1-dioxide monohydrate, (III) (Dupont, de Tullio, Pirotte, Masereel & Delarge, 1995). The presence of the 3-amino group in (I) instead of the 3-*tert*-butyl group in (II) or the 3-methyl group in (III) results in a lengthening of the N2—C3 bond.

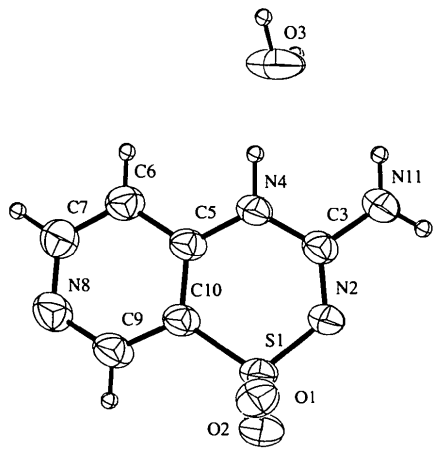

Fig 1. Molecular structure of (I) with the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level; H atoms are drawn as small circles of arbitrary radii.

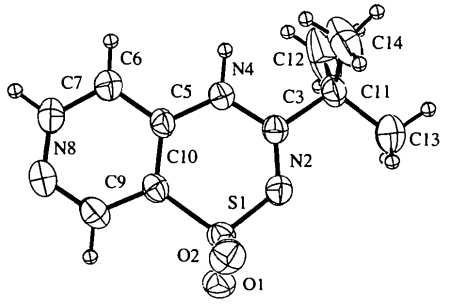

Fig 2. Molecular structure of (II) with the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level; H atoms are drawn as small circles of arbitrary radii.

Experimental

Compounds (I) and (II) were synthesized as described by Pirotte *et al.* (1993, 1995) at the Laboratory of Medicinal Chemistry, Liège. Crystals of (I) were obtained by slow evaporation of a water–methanol solution (75/25% by volume) at room temperature. Crystals of (II) were grown by slow evaporation of a methanol solution at room temperature.

Compound (I)

Crystal data

$C_6H_6N_4O_2S.H_2O$
M_r = 216.22
Monoclinic
$P2_1/a$
a = 7.487 (2) Å
b = 15.470 (7) Å
c = 8.131 (7) Å
β = 109.55 (3)°
V = 887.5 (9) Å^3
Z = 4
D_x = 1.618 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 21 reflections
θ = 18.55–34.66°
μ = 3.208 mm^{-1}
T = 293 (2) K
Prism
0.38 × 0.11 × 0.08 mm
Colourless

Data collection

Stoe Siemens AED four-circle diffractometer
ω scans
Absorption correction: ψ scan
T_{min} = 0.5820, T_{max} = 0.7014
1219 measured reflections
1219 independent reflections
964 observed reflections [$I > 2\sigma(I)$]
θ_{max} = 59.19°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 16$
$l = -9 \rightarrow 8$
2 standard reflections
frequency: 60 min
intensity decay: 2.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0342
$wR(F^2)$ = 0.1002
S = 1.173
1219 reflections
130 parameters
H atoms were constrained and included as riding atoms, except for the 4*H*-atom and water H atoms, which were kept fixed
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2 + 0.1258P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.179 e Å^{-3}
$\Delta\rho_{min}$ = −0.260 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0104 (11)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Compound (II)

Crystal data

$C_{10}H_{13}N_3O_2S$
M_r = 239.29
Monoclinic
$P2_1/a$
a = 9.802 (9) Å
b = 11.682 (9) Å
c = 10.384 (16) Å
β = 108.00 (10)°
V = 1130.9 (23) Å^3
Z = 4
D_x = 1.405 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 24 reflections
θ = 24.47–39.93°
μ = 2.477 mm^{-1}
T = 293 (2) K
Prism
0.38 × 0.38 × 0.15 mm
Colourless

Data collection

Stoe Siemens AED four-circle diffractometer
ω scans
Absorption correction: ψ scan
T_{min} = 0.3774, T_{max} = 0.6191
1566 measured reflections
1566 independent reflections
1388 observed reflections [$I > 2\sigma(I)$]
θ_{max} = 59.08°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -11 \rightarrow 10$
2 standard reflections
frequency: 60 min
intensity decay: 3.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0443$
$wR(F^2) = 0.1276$
$S = 1.160$
1566 reflections
151 parameters
H atoms were constrained and included as riding atoms, except for the 4*H*-atom, which was kept fixed
$w = 1/[\sigma^2(F_o^2) + (0.0785P)^2 + 0.6684P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.348$ e Å^{-3}
$\Delta\rho_{min} = -0.379$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0151 (13)
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}
(I)				
S1	0.24943 (9)	0.12782 (4)	0.16130 (9)	0.0456 (3)
N2	0.2255 (3)	0.04719 (13)	0.0360 (3)	0.0490 (6)
C3	0.3235 (4)	−0.0248 (2)	0.0870 (3)	0.0420 (6)
N4	0.4828 (3)	−0.03139 (12)	0.2284 (3)	0.0447 (6)
C5	0.5669 (3)	0.0382 (2)	0.3308 (3)	0.0405 (6)
C6	0.7434 (4)	0.0300 (2)	0.4585 (3)	0.0491 (7)
C7	0.8217 (4)	0.1002 (2)	0.5587 (4)	0.0543 (7)
N8	0.7384 (3)	0.1786 (2)	0.5387 (3)	0.0587 (7)
C9	0.5699 (4)	0.1862 (2)	0.4157 (4)	0.0524 (7)
C10	0.4773 (4)	0.1181 (2)	0.3118 (3)	0.0425 (6)
N11	0.2716 (3)	−0.09588 (14)	−0.0086 (3)	0.0537 (6)
O1	0.1171 (3)	0.12294 (12)	0.2549 (2)	0.0559 (6)
O2	0.2377 (3)	0.20555 (12)	0.0616 (3)	0.0625 (6)
O3	0.6519 (4)	−0.18460 (15)	0.2380 (3)	0.0813 (8)
(II)				
S1	0.03391 (7)	0.74648 (6)	0.47417 (7)	0.0379 (3)
N2	0.1468 (2)	0.7118 (2)	0.6157 (2)	0.0425 (6)
C3	0.2240 (3)	0.6198 (2)	0.6332 (3)	0.0360 (6)
N4	0.2310 (2)	0.5483 (2)	0.5326 (2)	0.0422 (6)
C5	0.1687 (3)	0.5710 (2)	0.3972 (3)	0.0370 (7)
C6	0.1943 (3)	0.5007 (3)	0.2987 (3)	0.0505 (8)
C7	0.1354 (3)	0.5315 (3)	0.1669 (3)	0.0569 (9)
N8	0.0563 (3)	0.6251 (3)	0.1236 (2)	0.0582 (7)
C9	0.0312 (3)	0.6893 (3)	0.2179 (3)	0.0504 (8)
C10	0.0818 (3)	0.6656 (2)	0.3552 (3)	0.0362 (7)
C11	0.3170 (3)	0.5889 (2)	0.7748 (3)	0.0414 (7)
C12	0.4725 (4)	0.5908 (5)	0.7787 (4)	0.099 (2)
C13	0.2895 (6)	0.6703 (4)	0.8771 (4)	0.108 (2)
C14	0.2787 (5)	0.4693 (4)	0.8082 (4)	0.0890 (14)
O1	0.0519 (2)	0.8658 (2)	0.4514 (2)	0.0516 (6)
O2	−0.1059 (2)	0.7128 (2)	0.4749 (2)	0.0527 (6)

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

	(I)		(II)
S1—O2	1.437 (2)		1.428 (2)
S1—O1	1.440 (2)		1.434 (2)
S1—N2	1.582 (2)		1.595 (3)
S1—C10	1.742 (3)		1.731 (3)
N2—C3	1.321 (3)		1.295 (4)
C3—N11	1.328 (3)	C3—C11	1.515 (4)
C3—N4	1.355 (3)		1.356 (4)
N4—C5	1.378 (3)		1.375 (4)
C5—C6	1.387 (4)		1.393 (4)
C5—C10	1.390 (3)		1.381 (4)
C6—C7	1.366 (4)		1.359 (5)
C7—N8	1.349 (4)		1.335 (4)
N8—C9	1.327 (4)		1.316 (4)
C9—C10	1.383 (4)		1.385 (4)
		C11—C13	1.511 (5)
		C11—C12	1.513 (5)
		C11—C14	1.514 (5)
O2—S1—O1	114.80 (12)		115.84 (13)
O2—S1—N2	108.92 (13)		108.6 (2)
O1—S1—N2	110.46 (12)		108.25 (13)
O2—S1—C10	109.24 (12)		108.99 (14)
O1—S1—C10	108.03 (13)		109.79 (14)
N2—S1—C10	104.92 (12)		104.8 (2)
C3—N2—S1	122.0 (2)		123.3 (2)
N2—C3—N11	119.4 (2)	N2—C3—C11	119.0 (2)
N2—C3—N4	124.6 (2)		124.7 (2)
N11—C3—N4	115.9 (2)	C11—C3—N4	116.3 (2)
C3—N4—C5	123.3 (2)		123.9 (2)
N4—C5—C6	120.6 (2)		120.9 (3)
N4—C5—C10	121.5 (2)		120.8 (2)
C6—C5—C10	117.9 (2)		118.3 (3)
C7—C6—C5	119.0 (3)		117.8 (3)
N8—C7—C6	123.7 (3)		125.3 (3)
C9—N8—C7	117.1 (2)		116.0 (3)
N8—C9—C10	123.3 (3)		124.2 (3)
C9—C10—C5	119.0 (3)		118.3 (3)
C9—C10—S1	122.4 (2)		122.4 (2)
C5—C10—S1	118.5 (2)		119.2 (2)
		C13—C11—C12	111.7 (4)
		C13—C11—C14	108.0 (3)
		C12—C11—C14	109.1 (3)
		C13—C11—C3	110.3 (3)
		C12—C11—C3	108.8 (3)
		C14—C11—C3	108.9 (2)
O2—S1—N2—C3	142.1 (2)		98.4 (3)
O1—S1—N2—C3	−90.9 (2)		−135.1 (2)
C10—S1—N2—C3	25.3 (2)		−18.0 (3)
S1—N2—C3—N11	166.3 (2)	S1—N2—C3—C11	−173.9 (2)
S1—N2—C3—N4	−17.2 (4)		7.5 (4)
N2—C3—N4—C5	−3.5 (4)		7.4 (4)
N11—C3—N4—C5	173.1 (2)	C11—C3—N4—C5	−171.2 (2)
C3—N4—C5—C10	10.1 (4)		−6.4 (4)
N4—C5—C10—S1	2.9 (3)		−7.7 (3)
O2—S1—C10—C5	−134.9 (2)		−98.3 (2)
O1—S1—C10—C5	99.5 (2)		133.9 (2)
N2—S1—C10—C5	−18.3 (2)		17.8 (2)

The values of the anisotropic displacement parameters of C12, C13 and C14 [compound (II), see Fig. 2] show that the *tert*-butyl group is slightly disordered.

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1988*a*); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1988*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

The authors thank M. M. Vermeire for his helpful assistance in the diffractometry measurements and the FNRS for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1238). 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). C**51**, 1388–1390

Urotropin-3-Diiod, $Ur.3I_2$

KARL-FRIEDRICH TEBBE UND KLAUS NAGEL

Institut für Anorganische Chemie, Universität zu Köln, Greinstraße 6, D-50939 Köln, Deutschland

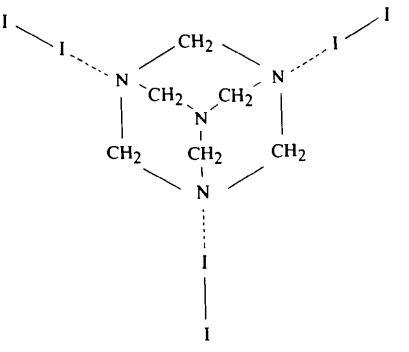
(*Eingegangen am* 3. *November* 1994; *angenommen am* 22. *Dezember* 1994)

Abstract

The structure of 1,3,5,7-tetraazatricyclo[3.3.1.$1^{3,7}$]-decane tris(diiodine), $C_6H_{12}N_4.3I_2$, has been determined. The high-symmetry compound belongs to the class of n–σ^* donor–acceptor complexes and shows the structural features of this group of compounds.

Kommentar

Bisher sind drei Molekülkomplexe $Ur.nI_2$ des Urotropins $C_6H_{12}N_4$ mit Iod I_2 für n = 1, 2, 3 beschrieben worden (Bowmaker & Knappstein, 1977), von denen die beiden iodärmeren $Ur.I_2$ und $Ur.2I_2$ auch strukturell als Donor-Akzeptor-Komplexe vom Typ n-σ^* charakterisiert werden konnten (Pritzkow, 1975*b*) und der iodärmste zusätzlich in ionischer Form $(Ur_2I)I_3$ als Triiodid des Bis(urotropin)iodonium-Kations auftreten kann (Bowmaker & Hannan, 1971; Pritzkow, 1975*a*). Durch Umsetzung von Urotropiniumiodid UrHI mit Iod I_2 läßt sich dagegen ein salzartiges Urotropiniumtriiodid $UrHI_3$ gewinnen (Tebbe & Nagel, 1995). Bei Versuchen zur Darstellung iodreicherer Polyiodide des Urotropiniumions $UrHI_n$ mit $n > 3$ durch Erhöhung des Iodangebots erhalten wir allerdings überraschend den bisher iodreichsten Molekülkomplex $Ur.3I_2$. Einer dreifachen Koordination durch Iod ist die Protonierung des Urotropins offensichtlich nicht mehr gewachsen. Die bisher fehlende Kristallstruktur des Molekülkomplexes haben wir zur Vervollständigung der Reihe ermittelt.



$Ur.3I_2$

Die Lageparameter sind in Tabelle 1 und die wichtigeren geometrischen Größen in Tabelle 2 aufgelistet. Die Bezeichnung der Atome geht aus Fig. 1 hervor.

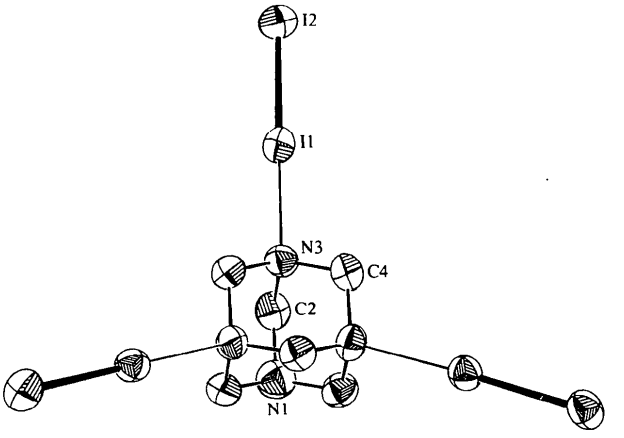


Fig. 1. Struktur der Baugruppen mit thermischen Ellipsoiden (50% Wahrscheinlichkeit) und den Atombezeichnungen. Auf eine Darstellung der H-Atome wurde zugunsten der Übersichtlichkeit verzichtet.

Strukturell lassen sich sämtliche Iodaddukte des Urotropins durch eine lineare Anordnung von Donoratom und Halogenmolekül charakterisieren, wobei das Halogenmolekül in Richtung des freien Elektronenpaars des Donoratoms ausgerichtet ist. Wie erwartet wird jeweils nach Knüpfung des kurzen Donor-Halogen-Abstands eine Streckung des Halogenmoleküls beobachtet.

In dem hier vorgestellten Molekülkomplex $Ur.3I_2$ der Symmetrie 3 liegt diesen Merkmalen entsprechend eine annähernd lineare Baueinheit N···I—I mit einseitig koordiniertem Iodmolekül vor. Die Bindungswinkel C—N···I an den Donor-N-Atomen bleiben wie bei den beiden Vergleichsstrukturen $Ur.I_2$ und $Ur.2I_2$ in der

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