References

Camerman, A. & Camerman, N. (1970). *Science*, **168**, 1457–1459.
Camerman, A. & Camerman, N. (1971). *Acta Cryst.* B**27**, 2205–2211.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Rogawski, M. A. & Porter, R. J. (1990). *Pharmacol. Rev.* **42**, 223–285.
Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
Stoe & Cie (1987*a*) *DIF*4. *Diffraction Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1987*b*) *EMPIR*. *Empirical Absorption Correction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1987*c*) *REDU*4. *Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1995). C**51**, 1903–1905

3-Benzamido-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

Pascal De Tullio, Bernard Pirotte,
Bernard Masereel and Jacques Delarge

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

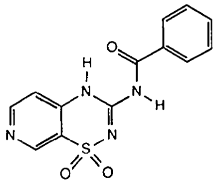
(*Received* 10 *January* 1995; *accepted* 17 *February* 1995)

Abstract

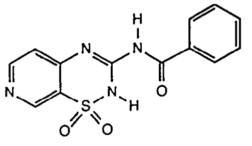
The title compound, $C_{13}H_{10}N_4O_3S$, is an original drug developed as a structural analogue of the anti-inflammatory agent piroxicam. It is also structurally related to diazoxide, an antihypertensive compound. The crystal structure determination shows that the 4*H* (rather than 2*H*) tautomeric form is preferentially adopted by this pyridothiadiazine derivative in the solid state.

Comment

3-Benzamido-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-dioxide is an original drug developed as a structural analogue of the anti-inflammatory agent piroxicam (4-hydroxy-2-methyl-*N*-(2-pyridyl)-2*H*-1,2-benzothiazine-3-carboxamide 1,1-dioxide). Moreover, the compound may be regarded as an acyl derivative of recently reported 3-alkylaminopyridothiadiazine dioxides (Pirotte *et al.*, 1993), known to be strong activators of the pancreatic ATP-sensitive potassium channel and structurally related to diazoxide [7-chloro-3-methyl-2*H*(or 4*H*)-1,2,4-benzothiadiazine 1,1-dioxide]. The particular interest of the present crystallographic study is to demonstrate which is the preferential tautomeric form adopted by the acyl derivative in the solid state: the 4*H* form (1) or the 2*H* form (2).



(1)



(2)

The values of the torsion angles show that the molecule is almost planar except for the phenyl moiety which is twisted by *ca* 40° [N11—C12—C13—C14 −141.0 (2)°] with respect to the rest of the molecule. There is an intramolecular hydrogen bond: N4···O3 2.643 (2), H4···O3 1.92 Å, N4—H4···O3 132°. The cohesion of the crystal is the result of van der Waals interactions and of one intermolecular hydrogen bond: N11···N8^{i} 2.908 (2), H11···N8^{i} 1.99 Å, N11—H11···N8^{i} 175° [symmetry code: (i) $-\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$]. The N2—C3 and N4—C3 bond lengths, the location of the H atom on N4 rather than on N2, and the hydrogen-bonding scheme, including the N4—H4···O3 intramolecular hydrogen bond, indicate that the 4*H* form rather than the 2*H* form is favoured in the crystal, confirming previous results obtained for the diazoxide (Bandoli & Nicolini, 1977) and for other thiadiazine derivatives, for example, 3-amino- and 3-*tert*-butyl-4*H*-pyrido[4,3-*e*]-1,2,4-thiadiazine 1,1-dioxide (Dupont, Pirotte, de Tullio, Masereel & Delarge, 1995).

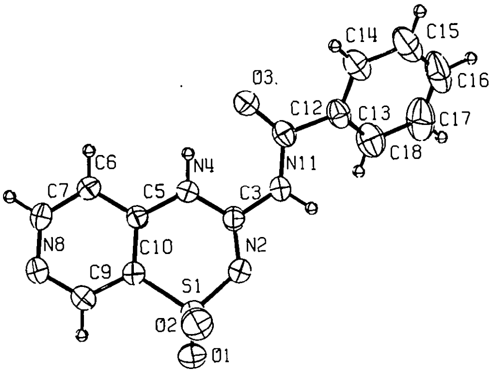


Fig 1. Molecular structure with atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as small circles of arbitrary radii.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995

Experimental

The title compound was synthesized as described by Pirotte *et al.* (1993) at the laboratory of Medicinal Chemistry of Liège. Crystals were obtained by slow evaporation of a methanol solution at room temperature.

Crystal data

$C_{13}H_{10}N_4O_3S$
$M_r = 302.31$
Monoclinic
$P2_1/n$
$a = 9.5563\ (3)$ Å
$b = 13.8791\ (8)$ Å
$c = 10.9290\ (8)$ Å
$\beta = 111.648\ (2)^\circ$
$V = 1347.30\ (13)$ Å^3
$Z = 4$
$D_x = 1.490$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 28 reflections
$\theta = 19.16–28.70^\circ$
$\mu = 2.301$ mm^{-1}
$T = 293\ (2)$ K
Prism
$0.46 \times 0.34 \times 0.15$ mm
Colourless

Data collection

Stoe Siemens AED four-circle diffractometer
ω-scans
Absorption correction: ψ scans (*EMPIR*; Stoe & Cie, 1987*b*)
$T_{\min} = 0.482$, $T_{\max} = 0.636$
1947 measured reflections
1842 independent reflections

1561 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0244$
$\theta_{\max} = 57.47^\circ$
$h = -9 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -11 \rightarrow 0$
2 standard reflections frequency: 60 min intensity decay: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0318$
$wR(F^2) = 0.0850$
$S = 1.109$
1842 reflections
191 parameters
H atoms constrained (riding) except the 4*H* atom (fixed)
$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 0.4485P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$

$\Delta\rho_{\max} = 0.182$ e Å^{-3}
$\Delta\rho_{\min} = -0.278$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0087 (5)
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)

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

	x	y	z	$U_{\rm eq}$
S1	0.16686 (6)	0.67598 (4)	0.74318 (5)	0.0442 (2)
N2	0.1711 (2)	0.72600 (12)	0.8765 (2)	0.0472 (5)
C3	0.2185 (2)	0.81378 (14)	0.9062 (2)	0.0360 (5)
N4	0.2934 (2)	0.86735 (11)	0.8474 (2)	0.0377 (4)
C5	0.3471 (2)	0.82899 (13)	0.7564 (2)	0.0341 (5)
C6	0.4481 (2)	0.87953 (15)	0.7152 (2)	0.0428 (5)
C7	0.4994 (3)	0.8359 (2)	0.6283 (2)	0.0495 (6)
N8	0.4651 (2)	0.74600 (14)	0.5826 (2)	0.0555 (5)
C9	0.3684 (3)	0.6987 (2)	0.6216 (2)	0.0520 (6)
C10	0.3046 (2)	0.73765 (14)	0.7051 (2)	0.0373 (5)
N11	0.1893 (2)	0.85481 (12)	1.0092 (2)	0.0389 (4)
C12	0.2373 (2)	0.94293 (15)	1.0661 (2)	0.0392 (5)
C13	0.1992 (2)	0.9642 (2)	1.1832 (2)	0.0440 (5)
C14	0.1553 (3)	1.0574 (2)	1.1993 (2)	0.0542 (6)
C15	0.1209 (3)	1.0805 (2)	1.3073 (3)	0.0717 (8)
C16	0.1311 (3)	1.0122 (3)	1.3997 (3)	0.0824 (10)
C17	0.1743 (3)	0.9197 (3)	1.3862 (2)	0.0814 (9)
C18	0.2096 (3)	0.8955 (2)	1.2776 (2)	0.0626 (7)
O1	0.2092 (2)	0.57737 (11)	0.7687 (2)	0.0668 (5)
O2	0.0248 (2)	0.69528 (13)	0.6416 (2)	0.0663 (5)
O3	0.3035 (2)	1.00087 (10)	1.02288 (15)	0.0494 (4)

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

S1—O1	1.425 (2)	N8—C9	1.326 (3)
S1—O2	1.427 (2)	C9—C10	1.381 (3)
S1—N2	1.601 (2)	N11—C12	1.372 (3)
S1—C10	1.744 (2)	C12—O3	1.221 (2)
N2—C3	1.298 (3)	C12—C13	1.483 (3)
C3—N4	1.348 (2)	C13—C18	1.381 (3)
C3—N11	1.378 (2)	C13—C14	1.391 (3)
N4—C5	1.383 (2)	C14—C15	1.375 (3)
C5—C10	1.385 (3)	C15—C16	1.362 (4)
C5—C6	1.396 (3)	C16—C17	1.374 (5)
C6—C7	1.361 (3)	C17—C18	1.389 (4)
C7—N8	1.340 (3)		
O1—S1—O2	116.90 (11)	N8—C9—C10	123.3 (2)
O1—S1—N2	109.17 (10)	C5—C10—C9	119.4 (2)
O2—S1—N2	108.91 (10)	C5—C10—S1	119.13 (14)
O1—S1—C10	109.45 (10)	C9—C10—S1	121.4 (2)
O2—S1—C10	107.93 (10)	C3—N11—C12	127.2 (2)
N2—S1—C10	103.67 (9)	O3—C12—N11	123.1 (2)
C3—N2—S1	121.58 (14)	O3—C12—C13	122.0 (2)
N2—C3—N4	126.6 (2)	N11—C12—C13	114.9 (2)
N2—C3—N11	115.8 (2)	C18—C13—C14	119.3 (2)
N4—C3—N11	117.7 (2)	C18—C13—C12	122.3 (2)
C3—N4—C5	122.3 (2)	C14—C13—C12	118.4 (2)
C10—C5—N4	120.8 (2)	C15—C14—C13	120.3 (3)
C10—C5—C6	117.6 (2)	C16—C15—C14	120.0 (3)
N4—C5—C6	121.5 (2)	C15—C16—C17	120.8 (3)
C7—C6—C5	118.2 (2)	C16—C17—C18	119.7 (3)
N8—C7—C6	125.0 (2)	C13—C18—C17	119.9 (3)
C9—N8—C7	116.4 (2)		
O1—S1—N2—C3	141.8 (2)	N4—C5—C10—S1	6.7 (3)
O2—S1—N2—C3	−89.5 (2)	O1—S1—C10—C5	−138.6 (2)
C10—S1—N2—C3	25.2 (2)	O2—S1—C10—C5	93.2 (2)
S1—N2—C3—N4	−12.9 (3)	N2—S1—C10—C5	−22.2 (2)
S1—N2—C3—N11	167.72 (14)	N2—C3—N11—C12	174.5 (2)
N2—C3—N4—C5	−8.8 (3)	C3—N11—C12—C13	−174.9 (2)
N11—C3—N4—C5	170.6 (2)	O3—C12—C13—C14	37.4 (3)
C3—N4—C5—C10	10.9 (3)	N11—C12—C13—C14	−141.0 (2)

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.

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: PA1176). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bandoli, G. & Nicolini, M. (1977). *J. Cryst. Mol. Struct.* **7**, 229–240.
Dupont, L., Pirotte, B., de Tullio, P., Masereel, B. & Delarge, J. (1995). *Acta Cryst.* **C51**, 1385–1388.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Pirotte, B., de Tullio, P., Lebrun, P., Antoine, M.-H., Fontaine, J., Masereel, B., Schynts, M., Dupont, L., Herchuelz, A. & Delarge, J. (1993). *J. Med. Chem.* **36**, 3211–3213.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
Stoe & Cie (1987*a*) *DIF4. Diffraction Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1987*b*) *EMPIR. Empirical Absorption Correction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1987*c*) *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1995). C**51**, 1905–1906

endo-2-Norborneol 2,4-Dinitrobenzoate

JONATHAN M. WHITE AND ALISON J. GREEN

School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

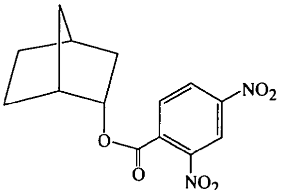
(*Received* 3 *November* 1994; *accepted* 16 *February* 1995)

Abstract

The structure of the title compound, $C_{14}H_{14}N_2O_6$ (*endo*-bicyclo[2.2.1]heptan-2-yl 2,4-dinitrobenzoate), was determined at 130 K to obtain an accurate measurement of the C—O bond length for comparison purposes. Steric interactions between the carboxyl function and the 2-nitro group of the ester result in these two groups twisting out of the plane of the aromatic ring. The C(alkyl)—O bond length is 1.465 (2) Å.

Comment

As part of our studies on the factors affecting C—O bond lengths (White & Robertson, 1992), we determined the structure of the title compound, (1), to obtain an accurate measurement of the C—O bond length for comparison purposes.



(1)

The X-ray data were measured at low temperature to remove the unwanted effects of thermal motion. The ester function exists in the *cisoid* conformation as defined by the torsion angle O2—C8—O1—C2 of −3.2 (2)°. Both the carboxyl and 2-nitro groups are rotated out of the plane of the phenyl ring; torsion angle O2—C8—C9—C14 is −34.7, O3—N1—C10—C9 is −51.6 (2) and O4—N1—C10—C11 is −53.7 (2)°. This acts to minimize steric interactions between these two substituents. The 4-nitro group is twisted slightly away from the plane of the phenyl ring; O5—N2—C12—C11 is 13.6 (2)°. The C(alkyl)—O bond length was determined to be 1.465 (2) Å.

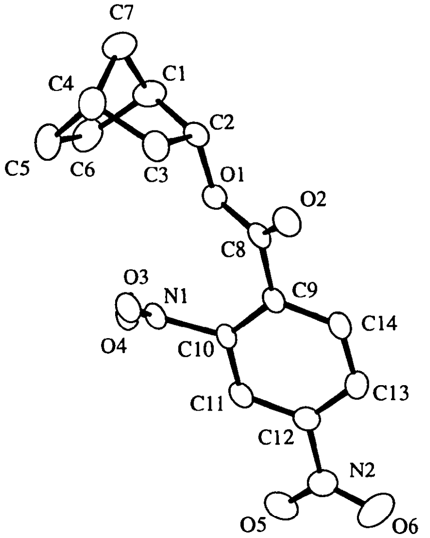


Fig. 1. *ORTEPII* (Johnson, 1976) drawing of (1). Displacement ellipsoids are shown at the 50% probability level.

Experimental

Crystals of (1) were obtained by slow evaporation from pentane.

Crystal data

$C_{14}H_{14}N_2O_6$
M_r = 306.27
Orthorhombic
Pbca
a = 9.0574 (9) Å
b = 11.658 (4) Å
c = 25.697 (4) Å
V = 2713.3 (11) Å^3
Z = 8
D_x = 1.500 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 13–17°
μ = 0.119 mm^{-1}
T = 130 (1) K
Block
0.57 × 0.50 × 0.27 mm
Colourless

Data collection

CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
4693 measured reflections
3946 independent reflections
3015 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0170
θ_{max} = 29.96°
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 16$
$l = -1 \rightarrow 36$
3 standard reflections
frequency: 160 min
intensity decay: 2%