

(Hall, Flack & Stewart, 1992). Molecular graphics: *Xtal ORTEP*. Software used to prepare material for publication: *Xtal BONDLA CIFIO*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: HU1133). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 1,2-Dihydrodipyrido[1,2-*b*:3',2'-*d*]-pyrazol-2-one

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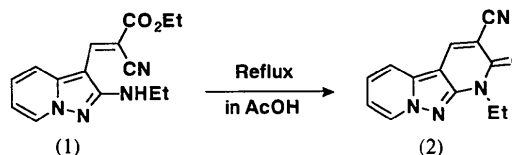
Abstract

The pyrazole and pyridine rings in the pyrazolo[1,5-*a*]-pyridine skeleton of 1-ethyl-2-oxo-1,2-dihydrodipyrido-[1,2-*b*:3',2'-*d*]pyrazole-3-carbonitrile, C₁₃H₁₀N₄O, are planar [maximum deviations 0.004 (3) and 0.004 (3) Å, respectively], and are almost coplanar to each other with

a dihedral angle of 0.9 (3)°. The planar 2-pyridone ring (fused to the pyrazolo[1,5-*a*]pyridine ring at the 2- and 3-positions) is also nearly coplanar with the pyrazolo-[1,5-*a*]pyridine ring [maximum deviation 0.032 (3) Å, dihedral angle 0.9 (3)°]. The delocalized ring system extends to the fused 2-pyridone ring.

Comment

The present study has been undertaken to confirm the chemical structure of the title compound, (2), and to compare the structural features of some nitrogen-bridged heterocycles such as pyrazolo[1,5-*a*]pyridines and fused pyrazolo[1,5-*a*]pyridine derivatives of physicochemical and pharmaceutical interest.



The title molecule is almost planar, except for the terminal C atom of the 1-ethyl group. The bond distances and angles for the pyrazolo[1,5-*a*]pyridine skeleton in the title compound are very similar to those in the geometry of 3-(*p*-chlorobenzoylthio)-2-(methylthio)pyrazolo[1,5-*a*]pyridine (Takehi, Kitajima, Ito & Takusagawa, 1994) and 2-acetyl-3-amino-5-ethylthieno[2',3':3,4]pyrazolo[1,5-*a*]pyridine (Takehi *et al.*, 1990). This indicates that the annelation of a six- or five-membered ring at the 2- and 3-positions of the pyrazolo[1,5-*a*]pyridine moiety does not result in a large difference in the bond distances and angles of the skeleton. On the other hand, the geometry of the attached pyridone ring, especially the lengthened N(1)—C(10) and C(2)—C(3) bonds, is somewhat different from that of the α -pyridone (Penfold, 1953), suggesting that the pyridone moiety in (2) has a different resonance structure from pyridone itself. This is a result of the fused pyrazolo[1,5-*a*]pyridine ring changing the resonance system of the pyridone ring.

The bond lengths and angles of the pyridine ring in the pyrazolo[1,5-*a*]pyridine moiety are similar to those in the indolizine derivatives, having no large distortions resulting from the annelation (Takehi, Kitajima, Ito & Takusagawa, 1993*a,b*). The bond lengths and angles of the pyrazole ring in the pyrazolo[1,5-*a*]pyridine moiety are also similar to those of the parent pyrazole (Ehrlich, 1960), except for the lengthened C(4)—C(5) bond, indicating that the pyrazole moiety of the title compound (2) also has a different resonance structure from pyrazole itself. There are no marked differences between the double and single bond lengths within the ring C atoms except for the C(1)—C(2) bond, showing the full extension of aromatic resonance over the ring system.

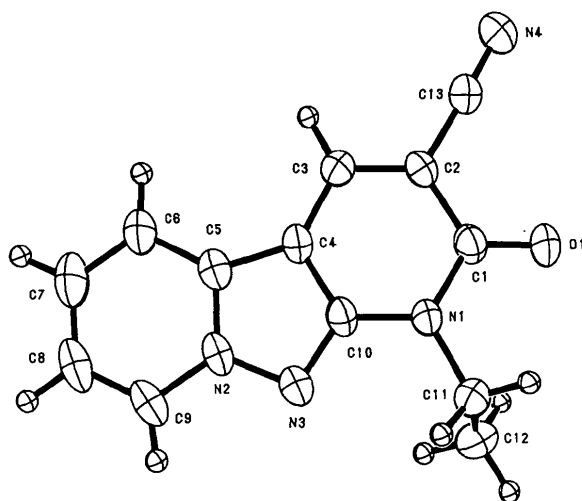


Fig. 1. ORTEP (Johnson, 1965) drawing of the title compound (2) showing the atomic numbering system. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

An acetic acid solution (30 ml) of ethyl 2-cyano-3-(2-ethylaminopyrazolo[1,5-*a*]pyridin-3-yl)acrylate (1) (100 mg, 0.35 mmol), which was prepared from the reaction of 1-[(ethylamino)methylthio]methyleneamino}-2-methylpyridinium iodide with ethyl (ethoxymethylene)cyanoacetate in the presence of a base at room temperature, was heated under reflux for 4 h. The hot reaction solution was immediately filtered and the filtrate was cooled to room temperature. The crystals (76 mg, 91%) of 1-ethyl-2-oxo-1,2-dihydropyrido[1,2-*b*:3',2'-*d*]pyrazole-3-carbonitrile (2) which were separated were collected by suction (Kakehi, Ito, Watanabe, Ono & Miyajima, 1980). For X-ray analysis, compound (2) was recrystallized from chloroform to give yellow needles.

Crystal data

$C_{13}H_{10}N_4O$

$M_r = 238.25$

Triclinic

$P\bar{1}$

$a = 8.382(3) \text{ \AA}$

$b = 14.457(4) \text{ \AA}$

$c = 4.868(3) \text{ \AA}$

$\alpha = 94.84(4)^\circ$

$\beta = 104.31(4)^\circ$

$\gamma = 77.68(2)^\circ$

$V = 558.1(4) \text{ \AA}^3$

$Z = 2$

$D_x = 1.418 \text{ Mg m}^{-3}$

Data collection

Rigaku AFC-5S diffractometer

ω - 2θ scans

Absorption correction: none

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 19.1\text{--}19.9^\circ$

$\mu = 0.089 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Needle

$0.60 \times 0.20 \times 0.16 \text{ mm}$

Yellow

$R_{int} = 0.041$

$\theta_{max} = 27.45^\circ$

$h = 0 \rightarrow 10$

$k = -17 \rightarrow 18$

$l = -6 \rightarrow 6$

2738 measured reflections
2559 independent reflections
1385 observed reflections
[$I > 3\sigma(I)$]

3 standard reflections
monitored every 150
reflections
intensity decay: 0.8%

Refinement

Refinement on F

$R = 0.046$

$wR = 0.054$

$S = 1.63$

1385 reflections

204 parameters

All H-atom parameters
refined

$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.19 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.21 \text{ e \AA}^{-3}$

Extinction correction:
analytical

Extinction coefficient:

0.98850×10^{-5}

Atomic scattering factors
from *International Tables*
for X-ray Crystallography
(1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
O(1)	0.0960 (2)	0.3015 (1)	−0.1138 (4)	3.7 (1)
N(1)	0.2659 (3)	0.3268 (2)	0.3185 (4)	2.9 (1)
N(2)	0.6079 (3)	0.2851 (2)	0.8901 (4)	3.2 (1)
N(3)	0.4662 (3)	0.3472 (2)	0.7511 (5)	3.5 (1)
N(4)	0.2181 (3)	0.0627 (2)	−0.3473 (6)	4.7 (1)
C(1)	0.2166 (3)	0.2699 (2)	0.0787 (5)	2.9 (1)
C(2)	0.3149 (3)	0.1738 (2)	0.0756 (5)	2.8 (1)
C(3)	0.4552 (3)	0.1407 (2)	0.2839 (6)	3.0 (1)
C(4)	0.5039 (3)	0.2025 (2)	0.5104 (5)	2.8 (1)
C(5)	0.6364 (3)	0.1973 (2)	0.7571 (6)	3.1 (1)
C(6)	0.7754 (4)	0.1294 (2)	0.8828 (7)	4.0 (2)
C(7)	0.8765 (4)	0.1526 (3)	1.1349 (7)	4.7 (2)
C(8)	0.8440 (4)	0.2423 (3)	1.2637 (7)	4.2 (2)
C(9)	0.7091 (4)	0.3088 (3)	1.1420 (6)	3.8 (2)
C(10)	0.4083 (3)	0.2941 (2)	0.5254 (5)	2.8 (1)
C(11)	0.1678 (4)	0.4232 (2)	0.3474 (7)	3.7 (1)
C(12)	0.2413 (5)	0.4974 (3)	0.2494 (9)	4.8 (2)
C(13)	0.2591 (3)	0.1133 (2)	−0.1616 (6)	3.3 (1)

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

O(1)—C(1)	1.231 (3)	C(2)—C(3)	1.376 (4)
N(1)—C(1)	1.398 (3)	C(2)—C(13)	1.434 (4)
N(1)—C(10)	1.382 (3)	C(3)—C(4)	1.395 (4)
N(1)—C(11)	1.474 (4)	C(4)—C(5)	1.415 (4)
N(2)—N(3)	1.388 (3)	C(4)—C(10)	1.399 (4)
N(2)—C(5)	1.377 (4)	C(6)—C(7)	1.369 (4)
N(2)—C(9)	1.371 (3)	C(5)—C(6)	1.399 (4)
N(3)—C(10)	1.336 (3)	C(7)—C(8)	1.395 (5)
N(4)—C(13)	1.145 (3)	C(8)—C(9)	1.361 (5)
C(1)—C(2)	1.457 (4)	C(11)—C(12)	1.507 (5)
C(1)—N(1)—C(10)	120.4 (2)	C(3)—C(4)—C(5)	135.5 (3)
C(1)—N(1)—C(11)	119.8 (2)	C(3)—C(4)—C(10)	120.1 (2)
C(10)—N(1)—C(11)	119.8 (2)	C(5)—C(4)—C(10)	104.4 (2)
N(3)—N(2)—C(5)	114.5 (2)	N(2)—C(5)—C(4)	104.6 (2)
N(3)—N(2)—C(9)	122.6 (3)	N(2)—C(5)—C(6)	118.7 (2)
C(5)—N(2)—C(9)	122.9 (3)	C(4)—C(5)—C(6)	136.8 (3)
N(2)—N(3)—C(10)	101.4 (2)	C(5)—C(6)—C(7)	118.7 (3)
O(1)—C(1)—N(1)	120.2 (3)	C(6)—C(7)—C(8)	121.1 (3)
O(1)—C(1)—C(2)	123.7 (2)	C(7)—C(8)—C(9)	120.5 (3)
N(1)—C(1)—C(2)	116.1 (2)	N(2)—C(9)—C(8)	118.1 (3)
C(1)—C(2)—C(3)	123.4 (2)	N(1)—C(10)—N(3)	122.9 (2)
C(1)—C(2)—C(13)	116.4 (2)	N(1)—C(10)—C(4)	121.9 (2)
C(3)—C(2)—C(13)	120.2 (3)	N(3)—C(10)—C(4)	115.1 (2)
C(2)—C(3)—C(4)	117.9 (3)	N(1)—C(11)—C(12)	112.3 (3)

The H atoms were located from a difference Fourier map and refined isotropically. The structure was solved by direct methods (SIR88; Burla *et al.*, 1989) utilizing the TEXSAN

(Molecular Structure Corporation, 1985) system. Molecular graphics were obtained using *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1131). 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[3,2-*e*][1,2,4]thiadiazine 1,1-Dioxide

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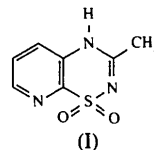
Abstract

The title compound, C₇H₇N₃O₂S, was prepared for comparison with diazoxide, an antihypertensive agent, from a structural and pharmacological point of view. The crystal structure determination shows that the 4*H*

tautomeric (rather than the 2*H*) form is preferentially adopted by this pyridothiadiazine derivative in the solid state.

Comment

The present structure, (I), is representative of a new class of heterocyclic compound, the 4*H*-pyrido[3,2-*e*][1,2,4]thiadiazine 1,1-dioxides, and was prepared for comparison with diazoxide from a structural and pharmacological point of view.



Diazoxide [7-chloro-3-methyl-2*H*(or 4*H*)-1,2,4-benzothiadiazine 1,1-dioxide] is a well known antihypertensive agent currently reported as the pharmacological reference compound for the benzothiadiazine class of ATP-sensitive potassium-channel openers (Edwards & Weston, 1990). The X-ray determination of the title compound may help in the identification of the preferential tautomeric form (the 2*H* or 4*H* tautomer) adopted by this pyridothiadiazine derivative in the solid state.

There are two independent molecules in the asymmetric unit. Molecules are linked by hydrogen bonds: N4—H4...N9ⁱ [(i) $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$] with N4...N9ⁱ 3.089 (5), H4...N9ⁱ 2.27 (5) Å, N4—H4...N9ⁱ 159.0 (2)° and N24—H24...N29ⁱⁱ [(ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$] with N24...N29ⁱⁱ 3.068 (5), H24...N29ⁱⁱ 2.23 (5) Å, N24—H24...N29ⁱⁱ 166.3 (2)°.

According to the bond lengths of N2—C3 and N4—C3 (N22—C23, N24—C23 in molecule *B*) and the hydrogen-bonding network, the 4*H* tautomeric form seems to be predominant in the crystal.

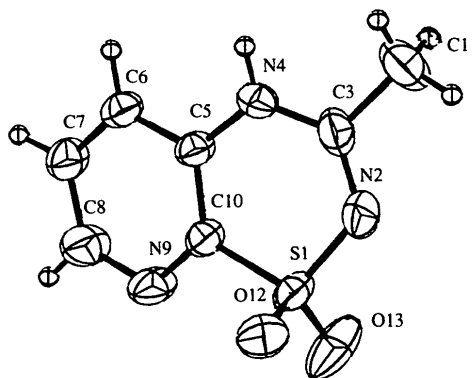


Fig. 1. Molecular structure with atom-labelling scheme of molecule A. (In molecule *B*, the atom numbering is incremented by 20.) Displacement ellipsoids are plotted at the 50% probability level.