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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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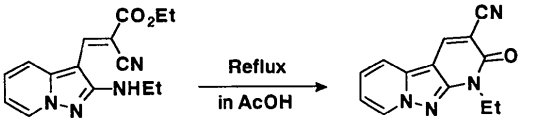
Abstract

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, $C_{13}H_{10}N_4O$, 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.



(1) (2)

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 (Kakehi, Kitajima, Ito & Takusagawa, 1994) and 2-acetyl-3-amino-5-ethyl-thieno[2′,3′:3,4]pyrazolo[1,5-*a*]pyridine (Kakehi *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 (Kakehi, 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.

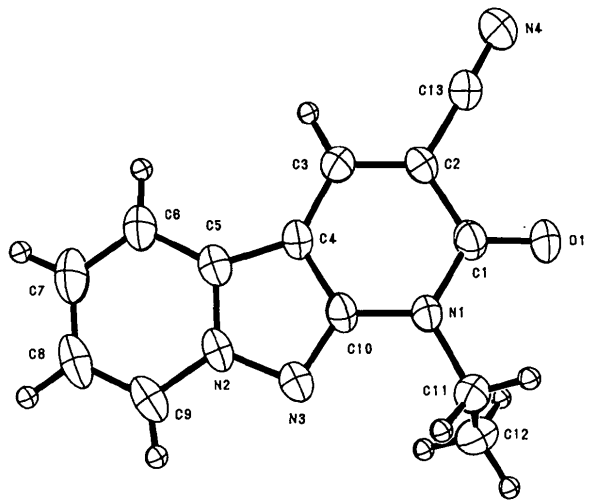


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound (2) showing the atomic numbering system. Displacement ellipsoids are drawn at the 50% probability level.

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-dihydrodipyrido-[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

$C_{13}H_{10}N_4O$	Mo $K\alpha$ radiation
M_r = 238.25	λ = 0.71069 Å
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	θ = 19.1–19.9°
a = 8.382 (3) Å	μ = 0.089 mm^{-1}
b = 14.457 (4) Å	T = 293 K
c = 4.868 (3) Å	Needle
α = 94.84 (4)°	0.60 × 0.20 × 0.16 mm
β = 104.31 (4)°	Yellow
γ = 77.68 (2)°	
V = 558.1 (4) Å^3	
Z = 2	
D_x = 1.418 Mg m^{-3}	

Data collection

Rigaku AFC-5*S* diffractometer	R_{int} = 0.041
ω–2θ scans	θ_{max} = 27.45°
Absorption correction: none	h = 0 → 10
	k = −17 → 18
	l = −6 → 6
2738 measured reflections	3 standard reflections
2559 independent reflections	monitored every 150 reflections
1385 observed reflections [$I > 3\sigma(I)$]	intensity decay: 0.8%

Refinement

Refinement on F	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
R = 0.046	$\Delta\rho_{min}$ = −0.21 e Å^{-3}
wR = 0.054	Extinction correction: analytical
S = 1.63	Extinction coefficient: 0.98850 × 10^{-5}
1385 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
204 parameters	
All H-atom parameters refined	
$w = 4F_o^2/\sigma^2(F_o^2)$	
$(\Delta/\sigma)_{max}$ = 0.01	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	B_{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* (Å, °)

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 (*SIR*88; 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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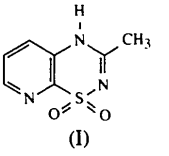
Abstract

The title compound, $C_7H_7N_3O_2S$, 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.



(I)

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···N9^{i} [(i) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$] with N4···N9^{i} 3.089 (5), H4···N9^{i} 2.27 (5) Å, N4—H4···N9^{i} 159.0 (2)° and N24—H24···N29^{ii} [(ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$] with N24···N29^{ii} 3.068 (5), H24···N29^{ii} 2.23 (5) Å, N24—H24···N29^{ii} 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.

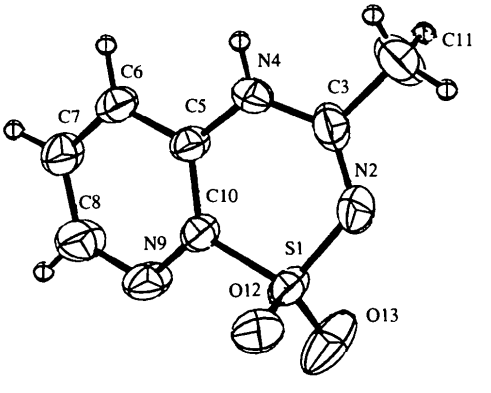


Fig. 1. Molecular structure with atom-labelling scheme of molecule *A*. (In molecule *B*, the atom numbering is incremented by 20.) Displacement ellipsoids are plotted at the 50% probability level.