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Ethyl 3-Cyano-6-methyl-2-oxo-4-(3-pyridyl)-3,4-dihydro-5-pyridinecarboxylate

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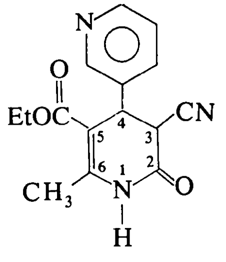
Abstract. $C_{15}H_{15}N_3O_3$, monoclinic, $P2_1/n$, a = 9·789 (2), b = 8·425 (2), c = 18·386 (3) Å, β = 103·70 (2)°, V = 1473·4 Å^3, Z = 4, D_c = 1·28 g cm^{-3}, μ(Cu $K\alpha$) = 7·7 cm^{-1}. The structure was solved by direct methods and refined to an R value of 0·058 for 1808 unique reflections. The investigated molecule exists in the keto form in the solid state. An intermolecular hydrogen bond, N(1)—H(1)···N(2*) = 2·866 (4) Å, is present.

Introduction. The structure of the title compound has been determined as a part of a study of potentially cytostatic compounds (Krajewski, Urbanczyk-Lipkowska & Gluzinski, 1977*a*,*b*) prepared by Nantka-Namirski & Balicki (1978).



The crystals were obtained by the action of ethyl acetoacetate on 2-cyano-3-(3-pyridyl)acrylamide (Nantka-Namirski & Balicki, 1972), and crystallized from ethyl alcohol.

A crystal of dimensions 0·3 × 0·25 × 0·28 mm was used for the collection of the data on a four-circle automated CAD-4 diffractometer (SLAF & BS, Kraków, Poland). Intensities were measured by the $\omega/2\theta$ scan technique up to $2\theta_{\max}$ = 120°, with graphite-monochromated Cu $K\alpha$ radiation.

1808 reflections with intensities $I > 2\sigma(I)$ were used for the structure determination and refinement. The structure was solved by direct methods using the XRAY 70 system (Stewart, Kundell & Baldwin, 1970) and refined by the full-matrix least-squares method with anisotropic thermal parameters to an R value of 0·058 (unit weights). Fractional coordinates for the non-hydrogen atoms are given in Table 1. The hydrogen atom coordinates were located from Fourier difference syntheses. Hydrogen atoms for the methyl and ethoxy groups were calculated. All hydrogen atoms were refined with a damping factor of 0·1. The refinement process was terminated when the maximum shift/error

Table 1. *Fractional coordinates* (×10⁴) *with e.s.d.'s in parentheses*

	x	*y*	*z*
C(1)	4348 (4)	3799 (4)	3847 (2)
C(2)	3879 (4)	3318 (4)	4444 (2)
C(3)	2354 (3)	3576 (4)	4452 (2)
C(4)	1881 (4)	5167 (4)	4057 (2)
C(5)	2217 (4)	5292 (4)	3294 (2)
O(1)	1469 (3)	5989 (3)	2765 (1)
N(1)	3459 (3)	4612 (4)	3261 (2)
C(6)	1418 (4)	2205 (4)	4094 (2)
C(7)	1645 (4)	1382 (4)	3488 (2)
N(2)	827 (3)	202 (4)	3139 (2)
C(8)	−270 (5)	−214 (5)	3412 (2)
C(9)	−578 (5)	534 (6)	4016 (3)
C(10)	268 (5)	1761 (5)	4361 (2)
C(11)	369 (4)	5491 (4)	3992 (2)
N(3)	−784 (3)	5717 (4)	3963 (2)
C(12)	5787 (4)	3532 (5)	3696 (2)
C(13)	4782 (4)	2448 (4)	5076 (2)
C(14)	4853 (5)	1331 (6)	6275 (2)
C(15)	4063 (5)	1590 (7)	6856 (2)
O(2)	5986 (3)	2035 (4)	5135 (1)
O(3)	4102 (3)	2174 (3)	5610 (1)

Table 2. *Refined hydrogen coordinates, with e.s.d.'s in parentheses*

Atom	Bonded to	*x*	*y*	*z*	$B_{\rm iso}$ (Å^2)
H(1)	N(1)	0·376 (5)	0·468 (5)	0·274 (2)	8·5 (1·2)
H(2)	C(3)	0·233 (4)	0·375 (4)	0·501 (2)	4·7 (0·9)
H(3)	C(4)	0·245 (4)	0·608 (4)	0·446 (2)	5·0 (0·9)
H(4)	C(7)	0·255 (4)	0·173 (5)	0·328 (2)	6·4 (1·0)
H(5)	C(8)	−0·087 (4)	−0·125 (5)	0·311 (2)	6·8 (1·1)
H(6)	C(9)	−0·136 (5)	−0·007 (5)	0·427 (2)	8·7 (1·3)
H(7)	C(10)	0·013 (5)	0·233 (5)	0·483 (2)	8·2 (1·2)
H(8)	C(12)	0·636 (5)	0·458 (6)	0·374 (2)	9·6 (1·4)
H(9)	C(12)	0·636 (5)	0·282 (6)	0·411 (2)	8·7 (1·3)
H(10)	C(12)	0·563 (5)	0·297 (6)	0·315 (3)	9·4 (1·3)
H(11)	C(14)	0·497 (5)	0·008 (6)	0·612 (3)	10·2 (1·5)
H(12)	C(14)	0·581 (5)	0·185 (6)	0·657 (3)	10·6 (1·5)
H(13)	C(15)	0·301 (4)	0·118 (5)	0·666 (2)	9·6 (1·2)
H(14)	C(15)	0·410 (4)	0·285 (5)	0·701 (2)	9·5 (1·2)
H(15)	C(15)	0·456 (4)	0·096 (5)	0·732 (2)	9·1 (1·2)

value was 0·016. The refined hydrogen coordinates are given in Table 2.* The numbering of the atoms is shown in Fig. 1, and bond distances and angles are given in Tables 3 and 4.

Discussion. The crystal structure analysis was undertaken to establish which of the two possible forms (keto or enolic) exists in the crystal.

Table 3. *Bond distances* (Å) *with e.s.d.'s in parentheses*

N(1)—C(1)	1·395 (4)	C(11)—N(3)	1·135 (3)
C(1)—C(2)	1·348 (5)	C(4)—C(5)	1·519 (5)
C(1)—C(12)	1·516 (6)	C(5)—O(1)	1·220 (4)
C(2)—C(13)	1·477 (5)	C(5)—N(1)	1·358 (5)
O(2)—C(13)	1·209 (5)	C(3)—C(6)	1·523 (5)
O(3)—C(13)	1·329 (5)	C(6)—C(7)	1·375 (5)
O(3)—C(14)	1·455 (5)	C(7)—N(2)	1·340 (4)
C(14)—C(15)	1·476 (7)	N(2)—C(8)	1·335 (6)
C(2)—C(3)	1·513 (5)	C(8)—C(9)	1·371 (7)
C(3)—C(4)	1·542 (5)	C(9)—C(10)	1·381 (6)
C(4)—C(11)	1·481 (5)	C(6)—C(10)	1·382 (6)

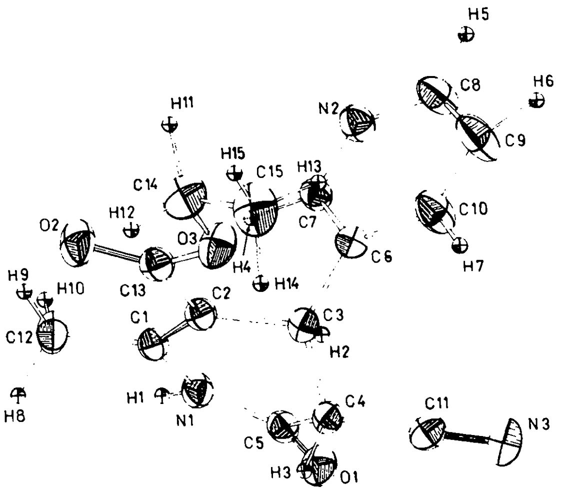


Fig. 1. *ORTEP* diagram (Johnson, 1965) of the molecule. Thermal ellipsoids are at the 40% probability level.

Table 4. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(5)—N(1)—C(1)	125·0 (3)	C(2)—C(13)—O(2)	127·0 (4)
N(1)—C(1)—C(2)	120·5 (3)	O(2)—C(13)—O(3)	122·1 (3)
N(1)—C(1)—C(12)	111·6 (3)	C(2)—C(13)—O(3)	110·9 (3)
C(12)—C(1)—C(2)	127·9 (3)	C(13)—O(3)—C(14)	117·6 (3)
C(1)—C(2)—C(13)	122·3 (3)	O(3)—C(14)—C(15)	106·8 (4)
C(3)—C(2)—C(13)	118·2 (3)	C(4)—C(11)—N(3)	177·8 (4)
C(1)—C(2)—C(3)	119·4 (3)	C(3)—C(6)—C(10)	120·6 (3)
C(2)—C(3)—C(4)	107·9 (3)	C(7)—C(6)—C(10)	116·9 (3)
C(2)—C(3)—C(6)	112·4 (3)	C(7)—C(6)—C(3)	122·4 (3)
C(4)—C(3)—C(6)	111·9 (2)	C(6)—C(7)—N(2)	124·7 (3)
C(3)—C(4)—C(5)	112·9 (3)	C(7)—N(2)—C(8)	117·2 (3)
C(3)—C(4)—C(11)	112·4 (3)	N(2)—C(8)—C(9)	122·3 (4)
C(11)—C(4)—C(5)	110·1 (3)	C(8)—C(9)—C(10)	119·5 (5)
C(4)—C(5)—N(1)	113·8 (3)	C(9)—C(10)—C(6)	119·3 (4)
C(4)—C(5)—O(1)	123·3 (3)	O(1)—C(5)—N(1)	122·8 (3)

The bond length C(5)—O(1) [for numbering see Fig. 1 (*ORTEP*, Johnson, 1965)] equal to 1·220 (4) Å is closer to the corresponding value of 1·222 Å in *p*-benzoquinone (Trotter, 1960) than to the C—O bond lengths 1·41, 1·35 or 1·36 Å observed in three independent phenol molecules (Gillier-Pandraud, 1967), thus supporting the keto form of the structure.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33595 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Least-squares planes*

The equations of the planes are in the form $Px + Qy + Rz = S$, where x,y,z are in Å in orthogonal space.

Plane	Atoms defining the plane	*P*	*Q*	*R*	*S*
(1)	C(1), N(1), C(2), C(5)	0·3334	0·9248	0·4567	6·5805
(2)	N(1), C(1), C(2), C(3)	0·1468	0·8747	0·4619	6·3701
(3)	C(2), C(13), O(2), O(3)	0·2299	0·8705	0·4353	6·3155
(4)	C(7), N(2), C(8), C(9), C(10), C(6)	0·4368	−0·6583	0·6131	3·0884

Distances of atoms from the planes (Å)

Plane (1)		Plane (2)		Plane (3)		Plane (4)	
C(1)	0·058	N(1)	0·008	C(2)	0·002	C(6)	0·000
N(1)	−0·060	C(1)	−0·017	C(13)	−0·006	C(7)	0·005
C(2)	0·058	C(2)	0·016	O(2)	0·002	N(2)	−0·006
C(5)	−0·028	C(3)	−0·007	O(3)	0·002	C(8)	0·002
C(3)	−0·342	C(4)	0·796	C(1)	0·055	C(9)	0·002
C(4)	0·344	C(5)	0·356	C(3)	−0·147	C(10)	−0·004
				C(14)	0·004		
				C(15)	0·409		

Table 6. *Torsion angles* (°) *in the dihydropyridine ring*

C(2)–C(1)–N(1)–C(5)	15·21
C(1)–N(1)–C(5)–C(4)	2·83
N(1)–C(5)–C(4)–C(3)	−36·86
C(2)–C(3)–C(4)–C(5)	51·31
C(1)–C(2)–C(3)–C(4)	−35·67
N(1)–C(1)–C(2)–C(3)	3·83

In the keto–enolic hybrid of 6-hydroxy-2-oxo-4-phenyl-3,5-pyridinedicarbonitrile (Pera, Tranqui, Fillion & Duc, 1975) the C—O bond length was found to be 1·25–1·27 Å.

The bond length N(1)—C(5) equal to 1·358 (5) Å is slightly longer than corresponding distances 1·349 (5) Å (average value) in *cyclo*(-L-Pro-L-Leu-) (Karle, 1972) and 1·343 (3) Å in 3,4-dehydroproline anhydride (Karle, Ottenheym & Witkop, 1974). The angle C(1)—N(1)—C(5) [125·0 (3)°] is greater than the corresponding angle in *cyclo*(-L-Pro-L-Leu-) [123·2 (3)°, average value] or in 3,4-dehydroproline anhydride [123·7 (2)°].

The C(1)—C(2) bond length [1·348 (5) Å] seems to be normal for the carbon–carbon double bond. The C(14)—C(15) distance in the ethoxycarbonyl chain appears to be shorter than normal [found to be 1·476 (7) Å]. This may be only partially explained as due to strong thermal vibrational motion. The libration-corrected distance is 1·479 Å, the correction being less than a half of the corresponding distance e.s.d.

The 3-pyridyl ring is planar (Table 5). The pyridinecarboxylate ring appears in a half-chair conformation [$C_2^{C(1)-N(1)}$ = 1·1°, see Table 6]. Considering the packing of the molecules in the unit cell, the intermolecular distance N(1)···N(2*) [N(2*) at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$] is found to be 2·866 (4) Å. The corresponding H(1)···N(2*) distance is 1·81 (5) Å and the N(1)—H(1)···N(2*) angle 169 (4)°. This indicates the presence of an intermolecular hydrogen bond, bridging the pyridyl- and dihydropyridinecarboxylate nitrogen atoms. Similar hydrogen bridges involving dihydropyridine nitrogen hetero-atoms were found in the cases of the 3,5-diacetyl and 3,5-diethoxycarbonyl derivatives of the 4-(3-pyridyl)dihydropyridine (Krajewski, Urbanczyk-Lipkowska & Gluzinski, 1977*a*,*b*) as well as in the 4-phenyl analogue of the latter compound (Mishnyov, Shvec, Bleidelis, Dubar, Sausin & Lusis, 1977).

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