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2-Methyl-4-oxo-3H,5H-6-imidazo[3,4-b]-[1,2,4]triazepinecarbonitrile: Condensation Product of a β-Keto Ester with 1,5-Diamino-4-imidazolecarbonitrile under Basic Conditions

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Abstract

In the triazepine, a double bond links atoms 1 and 2 [C=N = 1.276 (3) Å] with no evidence of an alternative tautomer in which the double bond is between 2 and 3 [C—C = 1.490 (4) Å]. ^{1}H NMR spectroscopy in d_6-DMSO confirms that this is the only tautomer present

in solution. A hydrogen bond between the triazepine N—H and the imidazo N atom in an adjacent molecule [N···N 2.950 (3), H···N 1.99 (2) Å, N—H···N 172 (2)°] links the molecules into infinite spirals along *b*.

Comment

Following our recent synthesis of 1,5-diamino-4-imidazolecarbonitrile in high yield (Alves, Booth, Freitas & Proença, 1992), we have undertaken a detailed study of its reactions with β-keto esters under basic conditions. It was clear from spectroscopic data that the reaction with sodium ethyl acetoacetate occurs by condensation of the 1- and 5-amino groups with both the keto and ester functions. However, it was impossible to decide from the available data whether the compound had structure (1) (formed by attack of the 1-amino group at the keto carbonyl and the 5-amino group at the ester carbonyl) or the alternative structure formed by inverting the ethyl acetoacetate group.

(1)
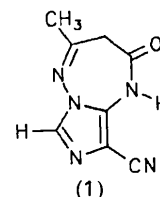
This work establishes (1) as the sole product in contrast to the finding of Bernardi, Viallefont & Zniber (1978) who reported that the reaction between 1,5-diamino-2-phenylimidazole and ethyl acetoacetate at the reflux temperature of xylene gives a mixture in which both the keto and ester carbonyls react with each of the amine substituents.
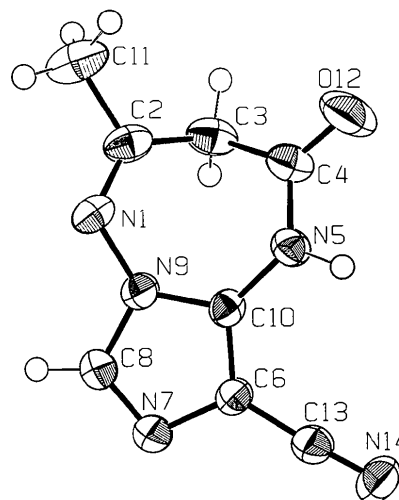

Fig. 1. The title molecule, showing atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976).

Experimental

Crystal data

$C_8H_7N_5O$	Mo $K\alpha$ radiation
$M_r = 189.18$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 20
$Pbca$	reflections
$a = 12.314$ (4) Å	$\theta = 14.5-25.0°$
$b = 10.274$ (3) Å	$\mu = 0.0929$ mm^{-1}
$c = 14.422$ (4) Å	$T = 296$ K
$V = 1824$ (1) Å^3	Needle
$Z = 8$	$0.30 \times 0.20 \times 0.20$ mm
$D_x = 1.377$ Mg m^{-3}	Colourless

Data collection

CAD-4 diffractometer	$h = -14 \rightarrow 14$
$\omega/2\theta$ scans	$k = 0 \rightarrow 11$
5791 measured reflections	$l = -16 \rightarrow 16$
1683 independent reflections	3 standard reflections
987 observed reflections	monitored every 150
$[I > 2\sigma(I)]$	reflections
$R_{int} = 0.027$	intensity variation: none
$\theta_{max} = 24.0636°$	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.21624$ e Å^{-3}
Final $R = 0.0437$	$\Delta\rho_{min} = -0.26029$ e Å^{-3}
$wR = 0.0425$	Extinction correction:
$S = 1.148$	Zachariasen type 2 Gaus-
987 reflections	sian isotropic
156 parameters	Extinction coefficient:
All H-atom parameters re-	18 (2) $\times 10^{-7}$
fined	Atomic scattering factors
Weighting scheme based on	from International Tables
measured e.s.d.'s	for X-ray Crystallography
$(\Delta/\sigma)_{max} = 0.0003$	(1974, Vol. IV)

Data collection: Enraf-Nonius diffractometer control. Cell refinement: Enraf-Nonius diffractometer control. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN; MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN; ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984).

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

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

	x	y	z	U_{eq}
N1	0.4144 (2)	0.6194 (2)	0.4940 (1)	0.0416
C2	0.3289 (2)	0.5518 (2)	0.4805 (2)	0.0429
C3	0.2527 (2)	0.5054 (3)	0.5536 (2)	0.0465
C4	0.3022 (2)	0.4080 (2)	0.6194 (2)	0.0449
N5	0.3875 (2)	0.4530 (2)	0.6709 (1)	0.0375
C6	0.4718 (2)	0.6540 (2)	0.7345 (1)	0.0367
N7	0.5101 (2)	0.7700 (2)	0.6979 (1)	0.0431
C8	0.4893 (2)	0.7630 (2)	0.6101 (2)	0.0420
N9	0.4393 (2)	0.6492 (2)	0.5868 (1)	0.0354
C10	0.4272 (2)	0.5784 (2)	0.6664 (1)	0.0319
C11	0.3034 (3)	0.5210 (4)	0.3813 (2)	0.0683
O12	0.2711 (2)	0.2972 (2)	0.6274 (2)	0.0750
C13	0.4789 (2)	0.6207 (2)	0.8299 (2)	0.0415
N14	0.4819 (2)	0.5893 (2)	0.9058 (1)	0.0583

Table 2. *Geometric parameters* (Å, °)

N1—C2	1.276 (3)	N5—C10	1.381 (3)
N1—N9	1.406 (2)	C6—N7	1.385 (3)
C2—C3	1.490 (4)	C6—C10	1.367 (3)
C3—C4	1.508 (4)	N7—C8	1.295 (3)
C4—N5	1.367 (3)	C8—N9	1.363 (3)
C2—N1—N9	116.3 (2)	N1—N9—C8	121.3 (2)
N1—C2—C3	125.9 (2)	N1—N9—C10	131.2 (2)
C2—C3—C4	113.7 (2)	C8—N9—C10	107.4 (2)
C3—C4—N5	115.4 (2)	N5—C10—C6	129.7 (2)
C4—N5—C10	124.2 (2)	N5—C10—N9	125.1 (2)
N7—C6—C10	110.6 (2)	C6—C10—N9	104.9 (2)
C6—N7—C8	104.9 (2)	C6—C13—N14	177.0 (2)
N7—C8—N9	112.2 (2)		

The title compound was prepared by addition of a solution of sodium ethyl acetoacetate in dry methanol to a solution of 1,5-diamino-4-imidazolecarbonitrile in the same solvent. The mixture was maintained at room temperature with stirring for 10 d, before neutralizing with acetic acid. Addition of silica gel and evaporation to dryness gave the product mixed with silica gel. This mixture was placed on top of a silica flash-chromotography column (silica GF$_{254}$ Fluka) and was eluted with acetone. Removal of the solvent from the eluate gave the product as off-white crystals (1.1 mmol, 61%). The product was fully characterized by microanalysis, ^{1}H and ^{13}C NMR and IR spectroscopy and mass spectrometry. The same compound can also be obtained by treatment of compound (2) (Booth, Pritchard, Freitas & Proença, 1993) with sodium methoxide in methanol followed by acidification.

(2)
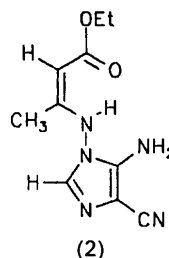
Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71218 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1045]

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