Crystal Structure of *N*-(4-Methyl-pyridin-2-yl)-3-oxo-butyramide

Sumati Anthal,* Prabhu Dutt,** N. K. Satti,** Rajnikant,* Vivek K. Gupta*†

*Post-Graduate Department of Physics and Electronics, University of Jammu, Jammu Tawi - 180 006, India
**Natural Products Chemistry Division, Indian Institute of Integrative Medicine, Jammu Tawi-180 001, India

The title compound, *N*-(4-methyl-pyridin-2-yl)-3-oxo-butyramide, $C_{10}H_{12}N_2O_2$, has been synthesized by condensing 2-amino-4-methylpyridine with ethylacetoacetate *via* microwave irradiation, and is one of the intermediates for the synthesis of pyrido[1,2-a]pyrimidin-2-one. The structure of the compound was established by spectral analysis and X-ray diffraction studies. The compound crystallizes in the orthorhombic space group $P2_12_12_1$ with unit-cell parameters: $a = 6.187(3)$, $b = 9.379(4)$, $c = 17.210(8)$Å, $Z = 4$. The crystal structure was solved by direct methods using single-crystal X-ray diffraction data, and refined to $R = 0.0527$ for 1739 observed reflections. The pyridine ring is planar with a maximum deviation of 0.002(3)Å observed for the atom C3′. The crystal packing is dominated by N–H···O, C–H···O, C–H···N hydrogen bonds and C–H–π interactions, which link the molecules into infinite chains.

The title compound belongs to the class of nitrogen heterocycles. Commonly employed reactions for the preparation of bridgehead and other related *N*-heterocycles are acid catalyzed interaction of hetaryl amines *viz.*, aminopyridines and aminopicolines, with 1,3-difunctional compounds *e.g.*, β-keto esters, malonates or 2-alkoxymethylene malonates. The interactions are known to proceed through the intermediacy of enamines, which are cyclized to the desired products *e.g.*, pyridopyrimidines, naphthyridines. The acetoacetylation of hetaryl and aryl amines by an interaction with ethyl acetoacetate (EAA) under microwave irradiation, in the absence of any catalyst or solvent, has been reported,[1] where the complete conversion of the amine into the *N*-acetoacetylated product resulted, without even a trace formation of enamine. Interactions of amines and EAA normally yield enamines, but in the above said process the ester carbonyl group reacts in preference to the ketone carbonyl group, and thus yields abnormal products. This constitutes the first observation regarding the acetoacetylation of –NH2 function using EAA. This reaction may prove to be of utility in synthetic organic chemistry. In the present communication, we report on X-ray studies of *N*-(4-methyl-pyridin-2-yl)-3-oxo-butyramide (Fig. 1), an acetoacetylated product of 2-amino-4-methyl pyridine, an intermediate involved in the synthesis of 2-oxo-2*H*-pyrido[1,2a]-pyrimidine.
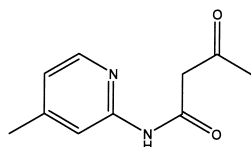
X-ray intensity data were measured by the ϕ and ω scan mode

for a θ range of 2.37 to 25.96°; 1739 reflections were treated as observed [$I > 2\sigma(I)$]. Data were corrected for Lorentz, polarisation and absorption factors. The structure was solved by direct methods using SHELXS97.[2] All non-hydrogen atoms of the molecule were located in the best E-map. A full-matrix least-squares refinement was carried out using SHELXL97.[2] All H atoms were geometrically fixed and allowed to ride on the corresponding non-H atoms with C–H = 0.93 – 0.97 Å, and U_{iso} = $1.5U_{eq}$ of the attached C atom for methyl H atoms and $1.2U_{eq}$ for other H atoms. The final refinement cycles converged to an $R = 0.0527$ and wR (F^2) = 0.1346 for the observed data. The

Fig. 1 Chemical structure of *N*-(4-methyl-pyridin-2-yl)-3-oxo-butyramide.

† To whom correspondence should be addressed.
E-mail: vivek_gupta2k2@hotmail.com

Table 1 Crystal and experimental data

Chemical formula: $C_{10}H_{12}N_2O_2$	
Formula weight: 192.22	
T = 100 K	
Crystal system: orthorhombic	Space group: $P2_12_12_1$
$a = 6.187(3)$Å	
$b = 9.379(4)$Å	
$c = 17.210(8)$Å	
$V = 998.6(8)$Å^3	$Z = 4$
D_x = 1.279 g/cm^3	D_m (floatation) = 1.286 g/cm^3
Radiation: Mo K_α (λ = 0.71073 Å)	
μ(Mo K_α) = 0.091 mm^{-1}	$F(0\ 0\ 0)$ = 408
Crystal size = $0.30 \times 0.20 \times 0.10$ mm^3	
No. of reflections collected = 5482	
No. of independent reflections = 1966	
θ range for data collection: 2.37 to 25.96°	
Data/Restraints/parameter = 1966/0/129	
Goodness-of-fit on F^2 = 1.008	
R indices [$I > 2\sigma(I)$]: $R1$ = 0.0527, $wR2$ = 0.1346	
R indices (all data): $R1$ = 0.0650, $wR2$ = 0.1650	
$(\Delta/\sigma)_{max}$ = 0.001 for tors H4A	
$(\Delta\rho)_{max}$ = 0.394 eÅ^{-3}	$(\Delta\rho)_{min}$ = –0.298 eÅ^{-3}
Measurement: Bruker SMART CCD area detector diffractometer.	
Programs system: SHELXL-97, SADABS	
Structure determination: SHELXS-97	
CCDC deposition number: 808457	

Table 2   Selected bond lengths (Å) and bond angles (°) for non-hydrogen atoms (e.s.d.'s are given in parentheses)

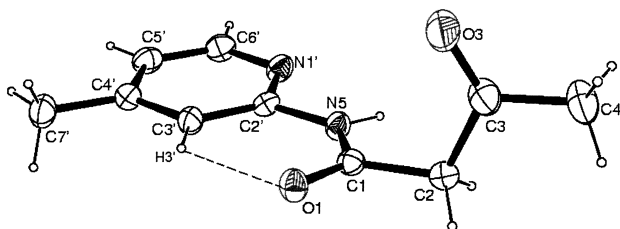| Bond lengths			
O1- C1	1.227(3)	N1' -C6'	1.340(4)
N1'- C2'	1.341(3)	N5- C1	1.356(3)
N5- C2'	1.414(3)	C3- O3	1.211(4)
Bond angles			
C6'- N1'- C2'	116.9(2)	C1- N5- C2'	128.8(2)
N1'- C2'- C3'	124.1(2)	N1'- C2'- N5	111.8(2)
C3'- C2'- N5	124.1(2)	N1'- C6'- C5'	123.3(3)
O1- C1- N5	124.4(2)	O1- C1- C2	121.8(2)
N5- C1- C2	113.7(2)	O3- C3- C4	122.0(3)
O3- C3- C2	121.6(3)		

Fig. 2   *ORTEP* view of the molecule with displacement ellipsoids drawn at 40% probability level. H atoms are shown as small spheres of arbitrary radii.
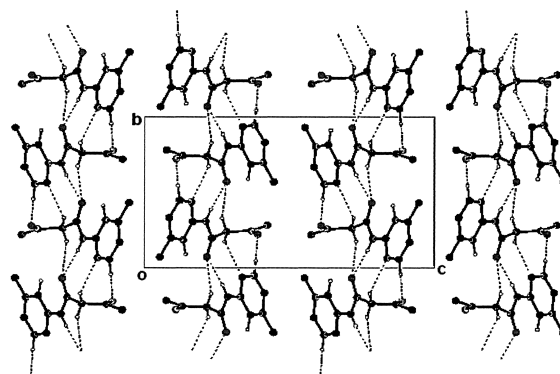

Fig. 3   The packing arrangement of molecules viewed down the *a*-axis.

and lengthening of the C1=O1 double bond is due to a strong intramolecular hydrogen bond between C3′ and O1. This intramolecular interaction leads to the formation of a pseudo six-membered ring comprising atoms O1, C1, N5, C2′, C3′ and H3′ having a planar conformation. There is a relative twist of the butyramide chain from planarity, with torsion angles C1–C2–C3–C4 and N5–C1–C2–C3 of 178.6(3) and 86.9(3)°, respectively. The butyramide group makes a dihedral angle of 41.1(1)° with the least-squares plane through the pyridine ring.

A packing view of the molecules in the unit cell viewed down the *a*-axis is shown in Fig. 3. The molecules are linked into infinite chains by N–H⋯O, C–H⋯N and C–H⋯O hydrogen bonds. One C–H⋯π hydrogen bond also exists. Chains of hydrogen-bonded molecules are packed with van der Waals contacts. Details of N–H⋯O, C–H⋯N, C–H⋯O and C–H⋯π hydrogen bonds are given in Table 3S. Synthesis and spectral details are deposited. See the journal site.

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residual electron densities ranged from –0.298 to 0.394 eÅ^{-3}. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4). The crystallographic data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2. An ORTEP view of the title compound with atomic labeling is shown in Fig. 2.[3] The geometry of the molecule was calculated using the WinGX[4] and PARST[5] software.

The bond lengths and bond angles are within the expected values.[6] The geometric parameters of pyridine ring are comparable to that normally found in pyridine and related molecules.[7,8] The six bond lengths in the pyridine ring lie in the range 1.340(4) – 1.394(4)Å with an average value of 1.372(4)Å. The bond angles in the pyridine ring vary from 116.9(2) to 124.1(2)° with an average of 120.0(2)°, which coincides exactly with the theoretical value of *sp*^{2} hybridization. The pyridine ring is perfectly planar, with a maximum deviation of 0.002(3)Å for C3′. The methyl group C7′ deviates by 0.022(3)Å from the least-squares plane of this ring.

The geometric parameters of the butyramide chain are comparable to that reported for butyramide.[9] The C–C bond lengths in the butyramide chain lie in the range 1.505(4) – 1.518(3)Å, and with N5–C1 and N5–C2′ bond lengths of 1.356(3) and 1.414(3)Å, respectively. The double bonds C1=O1 and C3=O3 are confirmed by their respective distances of 1.227(3) and 1.211(4)Å. The length of the double-bond C1=O1 is larger than the standard value for the carbonyl group, 1.192 Å

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