CROATICA CHEMICA ACTA CCACAA 53 (3) 435—440 (1980)

CCA-1221

YU ISSN 0011-1643
UDC 541.6:547.83
Original Scientific Paper

The Crystal and Molecular Structure of 3-(Pyridyl-2')--imidazo-[1,5-a] Pyridine

L. Golič, I. Leban, B. Stanovnik, M. Tišler, and A. Tomažič*

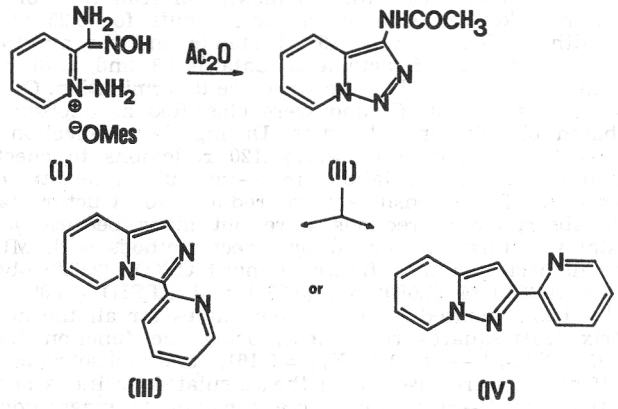
Chemistry Department, E. Kardelj University, 61001 Ljubljana, Slovenia, P.O.B. 537, Yugoslavia

Received March 17, 1980

The crystal structure of 3-(pyridyl-2')-imidazo-[1,5-a] pyridine has been determined using three-dimensional MoK α diffractometer data. The crystal data at 293 (1) K are as follows: $C_{12}H_9N_3$, M_r = = 195.23, orthorhombic, $P2_12_12_1$ (No. 19), a = 0.5107(1), b = 1.3076(2), c = 1.4343(3) nm, V = 0.9578 nm^3, D_m = 1.37(5), D_x = 1.354 Mg · m^{-3}, Z = 4. The structure has been solved with direct methods and refined by full-matrix least-squares techniques to R and R_w values of 0.085 and 0.080, respectively, for 641 contributing reflexions. The crystal structure consists of discrete molecules. Most of the bond lengths and angles are within normal ranges for aromatic heterocyclic systems. The dihedral angle between the pyridine and imidazo-pyridine parts of the molecule is 3.8°; thus the molecule is planar to within 7 pm owing to two weak C—H ... N interactions.

INTRODUCTION

In view of our continuing interest in the chemistry of azoloazines with bridgehead nitrogen, 1-acetylamino-*vic*-triazolo[1,5-a] pyridine (II) was recently prepared from 1-amino-2-carboxamidoximo-pyridinium mesitylenesulphonate (I). If the bicyclic compound (II) was heated either in a solution of hydrochloric acid in ethanol (50 wt-%) or in aqueous sodium bicarbonate, a compound was formed which according to the analytical and spectroscopic data would correspond to either the proposed structure (III) or (IV). Because



* To whom correspondence should be addressed.

of this structural ambiguity, a complete three — dimensional X-ray analysis was performed.

EXPERIMENTAL

The title compound crystallizes as transparent fragile needles from ethanol. It was difficult to select a crystal with good scattering properties. The systematic absences ($h00 : h = 2n + 1$; $0k0 : k = 2n + 1$; $00l : l = 2n + 1$) on Weissenberg photographs and the acentric values $< | E^2 - 1 | > = 0.764$ and $< | E | > = 0.883$ indicate the space group $P2_12_12_1$ (No. 19). Precise unit-cell dimensions were obtained from a least-squares fit of the 2Θ values of 45 reflexions measured on a CAD-4 diffractometer [MoK α_1 radiation, $\lambda = 70.926$ pm, $t = 293(1)$ K]. The density was measured by flotation. The crystal data are given in Table I.

TABLE I

Crystal Data for 3-(Pyridil-2')-imidazo-[1,5-a] Pyridine

Molecular formula	$C_{12}H_9N_3$
Molecular weight	195.23
Crystal symmetry	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a	0.5107(1) nm
b	1.3076(2) nm
c	1.4343(3) nm
Volume	0.9578 nm^3
D_m	1.37(5) Mg · m^{-3}
Z	4
D_x	1.354 Mg · m^{-3}
X-rays	MoK $\bar{\alpha}$ [$\lambda = 71.069$ pm]
μ (MoK α)	0.092 mm^{-1}

A needle-shaped single crystal with approximate dimensions $0.1 \times 0.1 \times 0.5$ mm, elongated along the [100] direction, was used for data collection on an automatic PDP8/M computer controlled Enraf-Nonius CAD-4 four-circle diffractometer with MoK α radiation equipped with a graphite monochromator. Reflexions were scanned in the $\omega - 2\Theta$ mode (moving crystal—moving counter) at different scan rates in order to obtain count of 5000 within a maximum scan time of 40 s. The background counts were taken at each of the scan limits for 0.25 of the scan time. The 2Θ scan width in degrees was $0.9 + 0.2 \tan\Theta$ and the aperture in mm was $2.5 + 0.9 \tan\Theta$. Two sets of diffractometer data (4008 and 1548 reflexions) were recorded, the smaller set was used in the structure determination. Of 1548 reflections, 907 had intensities less than $3\sigma(I)$ and were classified as unobserved. The values of $\sigma(I)$ were based on counting statistics. During data collection, the reflexions 1-1 2, 1 3 1, 1-3 1 were monitored every 120 reflexions to check for drifts in electronics, radiation damage, variations in X-ray tube intensity, crystal stability and counter response. The intensities were reduced to structure-factor moduli in the usual way. Absorption corrections were not made because μ (MoK α) = 0.092 mm^{-1}. The crystal structure was solved by direct methods with MULTAN 78[1]. An E map with the highest combined figure of merit CFOM (2.986) obtained with the unit weighting of ABSFOM (1.080), ψ_0 (0.877) and RESID (35.00), computed with 188 phases ($| E | > 1.20$), resulted in initial coordinates for all the heavy atoms. Isotropic full-matrix least-squares refinement, using the function $\Sigma w (| F_o | - | F_c |)^2$, proceeded to $R = \Sigma (|F_o| - |F_c|)/\Sigma |F_o| = 0.161$, and anisotropic refinement to $R = 0.105$. The H atoms were inserted in the calculated positions and refined under the constraint that the C—H vectors were constant in magnitude (108 pm) and direction but not in position (riding model). A common isotropic temperature factor

B for H atoms was refined to 0.060(8) nm². The final conventional R was 0.085, with $R_w \Sigma w^{1/2} | F_o | = 0.080$; the weighting scheme was $w = 1.00/[\sigma^2 (F_o) + 0.018 F_o^2]$. The final difference synthesis revealed no peak higher than 0.4 eÅ^{-3}. In the final refinement cycle, the average and maximum shift/error for the atomic parameters were 0.021 and 0.084, respectively, for U_{11} of C(6). All calculations were carried out on the CDC CYBER 172 computer at RRC Ljubljana with the SHELX 76 System of computer programs[5]. Atomic scattering factors for H were taken from reference 3 and for other atoms from reference 4. Lists of structure factors and thermal parameters are available on request.

Final atomic coordinates with $U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$ are given in Table II. The numbering of atoms is in agreement with the IUPAC convention.

TABLE II

Fractional Atomic Coordinates (× 10⁴ for C, N; × 10³ for H) and Equivalent Isotropic Thermal Parameters (× 10 nm²) with Estimated Standard Deviations

	x	y	z	U_{eq}
C(1)	—1508(23)	3536(8)	3035(8)	54(7)
N(2)	453(18)	4204(6)	2796(6)	53(6)
C(3)	725(20)	4828(7)	3487(6)	36(5)
N(4)	—965(17)	4625(5)	4172(5)	35(5)
C(5)	—1447(20)	5058(7)	5043(8)	43(6)
C(6)	—3411(23)	4711(8)	5602(8)	57(7)
C(7)	—4978(22)	3854(8)	5319(9)	56(7)
C(8)	—4506(22)	3416(9)	4452(9)	59(7)
C(8A)	—2433(23)	3773(7)	3869(7)	44(6)
N(1')	2665(15)	6316(6)	4192(6)	43(5)
C(2')	2662(20)	5666(7)	3494(7)	37(6)
C(3')	4380(21)	5746(8)	2740(8)	48(7)
C(4')	6197(22)	6549(8)	2743(9)	58(8)
C(5')	6257(23)	7187(8)	3491(8)	49(7)
C(6')	4500(24)	7084(8)	4160(8)	51(7)
H(1)	—221	292	260	
H(5)	—24	568	529	
H(6)	—381	509	626	
H(7)	—645	354	578	
H(8)	—575	281	420	
H(3')	428	520	217	
H(4')	753	665	217	
H(5')	774	777	354	
H(6')	446	764	472	

RESULTS AND DISSCUSION

Figure 1 shows a molecule viewed along the normal to the mean plane. Bond distances and angles are given in Table III. The results of the crystal structure determination show that the molecule exists as 3-(pyridyl-2')-imidazo[1,5-a] pyridine, the proposed compound III. The imidazo-pyridine and pyridine parts of the molecule are planar and are described by the equations

$$-0.6540\,X + 0.6252\,Y - 0.4259\,Z = 155.9 \text{ pm}$$

and

$$0.6477\,X - 0.5907\,Y + 0.4813\,Z = -109.7 \text{ pm},$$

where

$$X = a\,X \sin\beta,\ Y = by,\ Z = a\,X \cos\beta + cz.$$

TABLE III

Interatomic Distances (pm) and Angles (°) with Estimated Standard Deviations

Bond distances and angles

N(2)—C(1)	137(1)	C(8)—C(7)	139(1)
C(8A)—C(1)	132(1)	C(8A)—C(8)	143(1)
C(3)—N(2)	129(1)	C(2')—N(1')	131(1)
N(4)—C(3)	133(1)	C(6')—N(1')	137(1)
C(2')—C(3)	148(1)	C(3')—C(2')	140(1)
C(5)—N(4)	139(1)	C(4')—C(3')	140(2)
C(8A)—N(4)	141(1)	C(5')—C(4')	136(1)
C(6)—C(5)	136(1)	C(6')—C(5')	132(1)
C(7)—C(6)	143(1)		

C(8A)—C(1)—N(2)	110(1)	N(4)—C(8A)—C(1)	106(1)
C(3)—N(2)—C(1)	107(1)	C(8)—C(8A)—C(1)	136(1)
N(4)—C(3)—N(2)	112(1)	C(8)—C(8A)—N(4)	118(1)
C(2')—C(3)—N(2)	123(1)	C(6')—N(1')—C(2')	117(1)
C(2')—C(3)—N(4)	125(1)	N(1')—C(2')—C(3)	119(1)
C(5)—N(4)—C(3)	134(1)	C(3')—C(2')—C(3)	118(1)
C(8A)—N(4)—C(3)	106(1)	C(3')—C(2')—N(1')	123(1)
C(8A)—N(4)—C(5)	120(1)	C(4')—C(3')—C(2')	118(1)
C(6)—C(5)—N(4)	122(1)	C(5')—C(4')—C(3')	119(1)
C(7)—C(6)—C(5)	120(1)	C(6')—C(5')—C(4')	119(1)
C(8)—C(7)—C(6)	119(1)	C(5')—C(6')—N(1')	124(1)
C(8A)—C(8)—C(7)	121(1)		

C—H . . . N interaction

C(5)—H(5)	108	C(3')—H(3')	108
N(1') . . . H(5)	231	N(2) . . . H(3')	252
C(5) . . . N(1')	293(1)	C(3') . . . N(2)	285(1)
C(5)—H(5)—N(1')	115	C(3')—H(3')—N(2)	96

The largest deviations from the planes are —3.5 pm for C(8A) and —2.6 pm for C(5'). The corresponding average deviations are 1.5 and 1.3 pm, respectively. The dihedral angle between the imidazopyridine and pyridine parts of the molecule is 3.8° thus the molecule as a whole is planar with the largest deviation of 7.2 pm for C(6'). Planarity is probably due to rather weak C—H . . . N interactions which link C(5)—H(5) . . . N(1') and C(3')—H(3') . . . N(2). The C(5) . . . N(1') and C(3') . . . N(2) distances are 293(1) and 285(1) pm, respectively. Because of moderate accuracy of the structure determination, it was not possible to locate precisely the H atoms and to give a complete description of these C—H . . . N interactions.

The bond distances are intermediate between double and single bonds, thus indicating the presence of considerable conjugation in the separate parts as well as in the molecule as a whole. The values for bond distances and angles are within normal ranges for aromatic heterocyclic systems[5].

Figure 2 shows the general features of the molecular packing in the unit cell of the crystal viewed along the [100] direction. There are no unusually close van der Waals contacts between the separate molecules.

Acknowledgement. — The financial support of the Research Community of Slovenia is gratefully acknowledged.

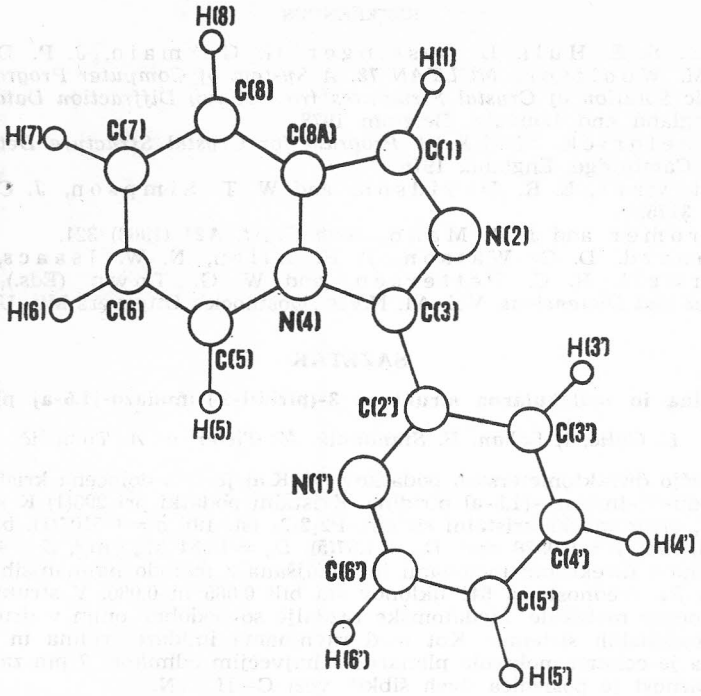


Figure 1. A schematic view of the molecule with the atomic numbering.

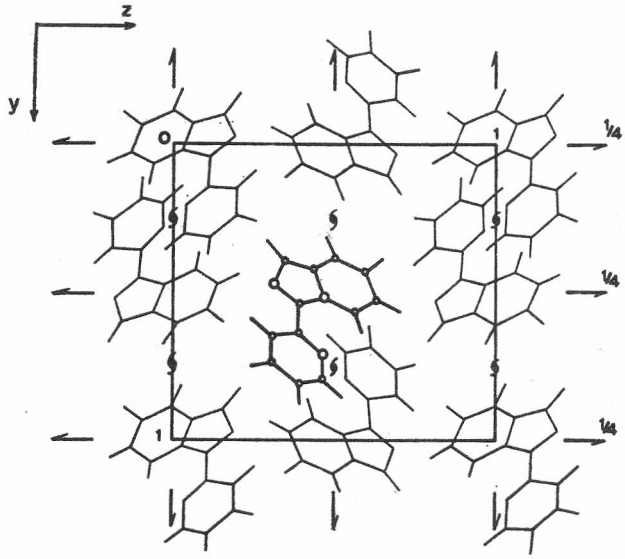


Figure 2. The molecular packing in the crystal. A projection along the [100] direction. The molecule drawn with bold-type bonds represents the crystal chemical unit whose coordinates are given in Table II.

REFERENCES

1. P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, *MULTAN* **78**. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England and Louvain, Belgium 1978.
2. G. M. Sheldrick, *SHELX* **76**. *Program for Crystal Structure Determination.* Univ. of Cambridge, England, 1976.
3. R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.* **42** (1965) 3175.
4. D. T. Cromer and J. B. Mann, *Acta Cryst.* **A24** (1968) 321.
5. O. Kennard, D. G. Watson, F. H. Allen, N. W. Isaacs, W. D. S. Motherwell, R. C. Pettersen, and W. G. Town (Eds.), *Molecular Structures and Dimensions*, Vol. A1, N.V.A. Oosthoek's Uitgevers Mij, Utrecht 1972.

SAŽETAK

Kristalna in molekularna struktura 3-(piridil-2')-imidazo-[1,5-a] piridina

L. Golič, I. Leban, B. Stanovnik, M. Tišler in A. Tomažič

S pomočjo difraktometerskih podatkov (MoK α) je bila določena kristalna struktura 3-(piridil-2')-imidazo-[1,5-a] piridina. Kristalni podatki pri 293(1) K so: $C_{12}H_9N_3$, $M_r = 195.23$, ortorombski kristalni sistem, $P2_12_12_1$ (št. 19), $a = 0.5107(1)$, $b = 1.3076(2)$, $c = 1.4343(3)$ nm, $V = 0.9578$ nm^3, $D_m = 1.37(5)$, $D_x = 1.354$ Mg · m^{-3}, $Z = 4$. Struktura je bila rešena z direktnimi metodami in izboljšana z metodo najmanjših kvadratov. Končni R i R_w vrednosti za 641 uklonov sta bili 0.085 in 0.080. V strukturi so prisotne posamezne molekule. Medatomske razdalje so podobne onim v drugih heterocikličnih aromatskih sistemih. Kot med ravninama imidazopiridina in piridina je 3.8° tako, da je celotna molekula planarna z največjim odmikom 7 pm za posamezen atom. Planarnost je posledica dveh šibkih vezi C—H ... N.

VTOZD KEMIJA IN KEMIJSKA TEHNOLOGIJA
UNIVERZA EDVARDA KARDELJA
61001 LJUBLJANA

Prispjelo 17. marca 1980.