# A NEW TETRACYCLIC SYSTEM-3*H*,10*H*- PYRAZOLO[4', 3': 5, 6] PYRIDO[4, 3- *B*]INDOLE

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**ABSTRACT** :- A 6, 7, 8, 9- tetrahydro derivative of a new heteroaromatic tetracyclic ring system – 3*H*,10*H*-pyrazolo[4',3': 5,6]pyrido[4,3-***b***]indole has been obtained from a Fisher-indolization of cyclohexanone hydrazone of IIb in excellent yield .

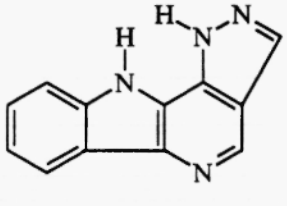
## INTRODUCTION

Among various possible isomeric pyrazolopyridoindoles, only one pyrazolo[3', 4': 4, 5]pyrido[3, 2-***b***]indole (I) has been reported in the literature and its various derivatives are claimed to have anticonvulsant, anxiolytic and sedative activities[1]. Now we would like to describe the synthesis of another isomer of (I) - ***3H,10H***-pyrazolo[4',3': 5,6]pyrido[4, 3-***b***]indole (III).

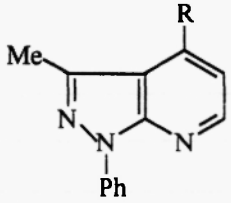
During the course of our work on the chemistry of pyrazolo[3, 4-***b***]pyridine system ,we had prepared its 4-chloro derivative which undergoes facile nucleophilic substitution[2,3]. In one of these reactions 4-hydrazino-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-***b***]pyridine, (IIb) was obtained in 77% yield from hydrazine hydrate and 4-chloro-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-***b***]pyridine(IIa).When cyclohexanone hydrazone of IIb was heated in diethylene glycol, it underwent a smooth fisher-indolization to afford the title ring system III in 70% yield. This was duly characterized through its elemental analysis,mass(m/z:302,52% M$^+$) and $^1$H NMR spectra.

The $^1$H NMR spectra displayed methylene signals between δ 1.60 and 2.96, appearance of a singlet at δ 8.62 with the disappearance of the H-5 proton signal at δ 6.58.

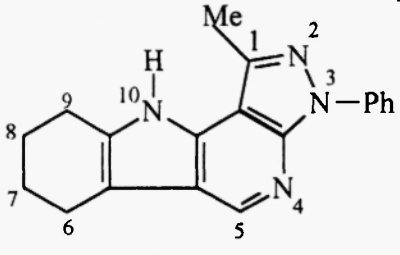
The Fisher- indolization of IIb was carried out under thermal conditions[4] to avoid protonation of pyridine nitrogen in the usual acid-catalyzed cyclization.



I



II a R=Cl
b R=NHNH$_2$



III

## EXPERIMENTAL

**4-Hydrazino-3-methyl-1-phenyl-1*H*-pyrazolo[3,4-*b*]pyridine (IIb)**

A mixture of IIa (4g),85% hydrazine hydrate (15 mL) and ethanol (30mL) was heated under reflux for 10 hrs.The reaction mixture was inverted over ice-water and the precipitate filtered, dried and crystallized from a mixture of benzene/ pet. ether (40-60°C) to give IIb,3g(77%);m p. 174-175°C.
*Anal.* Calcd. for $C_{12}H_{13}N_5$: C, 65.25; H, 5.47; N, 29.27.Found: C, 65.09; H, 5.57; N, 29.00.
$^1$H NMR($CDCl_3$): δ 2.68( s,3H,$CH_3$); 3.6-3.88 to 6.18-6.40(br.,3H, $NHNH_2$); 6.58(d,1H,$J_{5,6}$=4.5Hz,H-5); 7.10-7.60 and 8.10-8.24(m, 5H, Ph) ;8.28 (d, 1H, $J_{5,6}$= 4.5 Hz,H-6).
IR (KBr) $cm^{-1}$ 3340 ( $NHNH_2$ str ), 1590, 1500, 1490, 1285, 870, 790, 760.
MS, $M^+$ = 239.

**1-Methyl-3-phenyl-6,7,8,9-tetrahydro-3*H*,10*H*-pyrazolo[4',3':5,6]pyrido[4,3-*b*]indole (III)**
A mixture of 0.6g of IIb , 0.25g of cyclohexanone, 0.6g of sodium acetate in 12mL of 30% ethanol was heated for an hour and the resulting hydrazone was extracted with 3 x 15mL of chloroform. The solvent was removed and the residue was taken up in 5mL of diethylene glycol , heated under reflux for one hour and diluted with 10mL of water. The precipitate was filtered, dried and crystallized from ethanol to yield III, 0.54g; 70% m.p. 258- 260°C .
*Anal.* Calcd. For $C_{19}H_{18}N_4$: C, 75.46; H, 6.00; N, 18.55.Found: 75.20; H, 5.92; N, 18.44.
$^1$H NMR($CDCl_3$): δ 1.60- 2.40 and 2.54- 2.96 (m, 8H, 4C$H_2$ ); 2.78(s, 3H, C$H_3$ ); 7.04- 7.60 and 8.04-8.34 (m, 5H, Ph), 8.62(s, 1H, H- 5).
IR(KBr)$cm^{-1}$: 3620, 3200 (NH str.); 2930, 1640.
MS, $M^+$ = 302.

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