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### **Anomalous Proton NMR Deshielding in Anilinopyrazoles**

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ANOMALOUS PROTON NMR DESHIELDING  
IN ANILINOPYRAZOLES

Key Words: Proton NMR, Through Space  
Deshielding, IR Spectra,  
UV Spectra.

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INTRODUCTION

In connection with the synthesis of thienobenzodiazepines and certain heterocyclic analogues<sup>1</sup>, a number of anilino heterocycle precursors were prepared. Their proton NMR spectra were generally unexceptional with the exclusion of one of the pyrazole isomers which showed a remarkable deshielding of one proton signal in the aniline ring. Further

investigations have inferred that this low field shift can be attributed to through space deshielding by a proximal pyrazole nitrogen lone pair.

### EXPERIMENTAL

Proton NMR spectra were recorded on a Varian FT80A spectrometer at 80 MHz using  $\text{CDCl}_3$  (99.8% isotopic purity) as solvent. Infrared and Ultraviolet absorption spectra were obtained on Perkin-Elmer 297 and Pye-Unicam SP800 spectrophotometers.

### RESULTS AND DISCUSSION

The assignment of proton NMR peaks to the anilino-pyrazole I (Figure 1) is readily deduced from the chemical shifts and coupling constants in model anilines and is found to be closely similar to other anilino-heterocycles in this series. Thus the signal for  $\text{H}_2$  at  $\delta = 6.45$  is consistent with its situation ortho to the electron releasing -NH- substituent in N-arylanilines. In contrast, the isomeric pyrazole II gave a proton spectrum which was almost identical to I except that the signal for  $\text{H}_2$  (to high field of the remainder of the

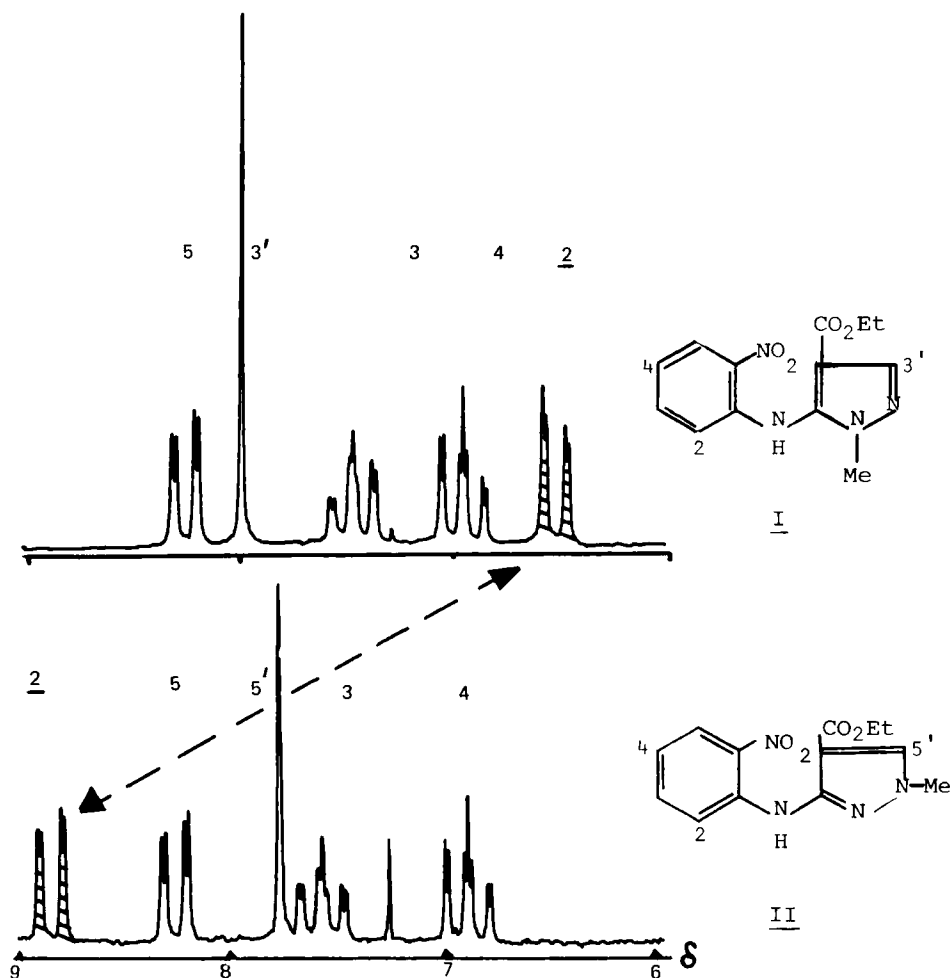


Figure 1. 80 MHz  $^1\text{H}$  NMR

Spectra of I and II (6-9 $\delta$ )

aromatic proton signals in I) was shifted by 2.3  $\delta$  to 8.73  $\delta$ , thus appearing to low field of the remaining aromatics (Figure 1).

This shifted signal was confirmed as  $\text{H}_2$  by examination

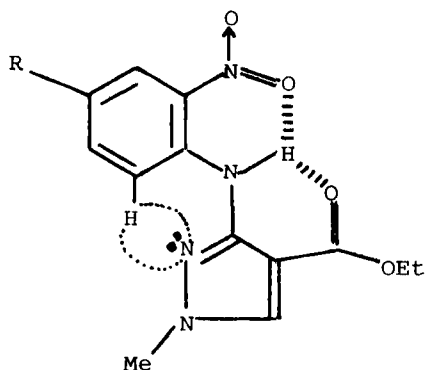


Figure 2

Hydrogen bonding in II

II, R = H

of the 4-chloro derivative (II below, R = Cl) in which  $H_2$  is reduced to a doublet with an ortho proton coupling of 8.8 Hz.

We believe that the 2.3  $\delta$  downfield shift arises because the entire molecule is held in an almost planar configuration by hydrogen bonding of the NH group with both the nitro and ester functions (Figure 2).

A molecular model of II shows that  $H_2$  closely approaches pyrazole N-2 (five bonds distant) and is within the powerful through space deshielding influence of its lone pair (dotted area). Through space interaction involving a pyrazole N-2 atom also accounts for the greater deshielding of the ortho phenyl protons of

Table. Infrared ( $\text{CHCl}_3$  solution) and Ultraviolet (MeOH solution) spectral data for isomeric pyrazoles I and II.

INFRARED ( $\text{cm}^{-1}$ )	I	II
$\nu(\text{C=O})$	1715	1695
$\nu(\text{N-H})$	3345	3320
ULTRAVIOLET (nm)		
$\lambda$ max	394	432

N-phenylpyrazole than those of N-phenylpyrrole<sup>2,3</sup> but the effect is very much smaller ( $0.3 \delta$ ).

The co-planar hydrogen bonded model we have proposed for II is further supported by Infrared and Ultraviolet spectrophotometric data. Hydrogen bonding would be expected<sup>4</sup> to lower the stretching frequencies of both the C=O and N-H bonds as indeed occurs (Table). The Ultraviolet absorption maximum for II is 38 nm higher than for I (in which co-planarity and extended conjugation is impeded by the N-methyl group).

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