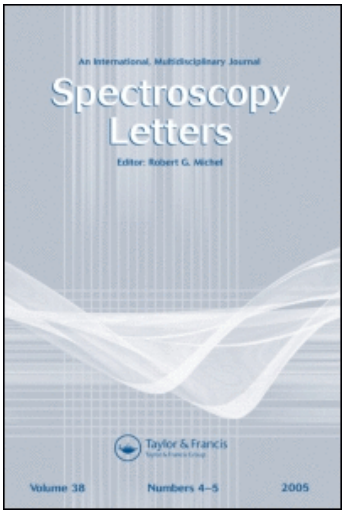

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Anomalous Proton NMR Deshielding in Anilinopyrazoles

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To cite this Article Rackham, David M. , Morgan, Sarah E. , Chabrabarti, Jiban K. and Hotten, Terrence M.(1980) 'Anomalous Proton NMR Deshielding in Anilinopyrazoles', Spectroscopy Letters, 13: 2, 159 — 164
To link to this Article: DOI: 10.1080/00387018008065079
URL: http://dx.doi.org/10.1080/00387018008065079

SPECTROSCOPY LETTERS, 13(2&3), 159-164 (1980)

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[1], 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 $CDCl_3$ (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 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 H_2 (to high field of the remainder of the

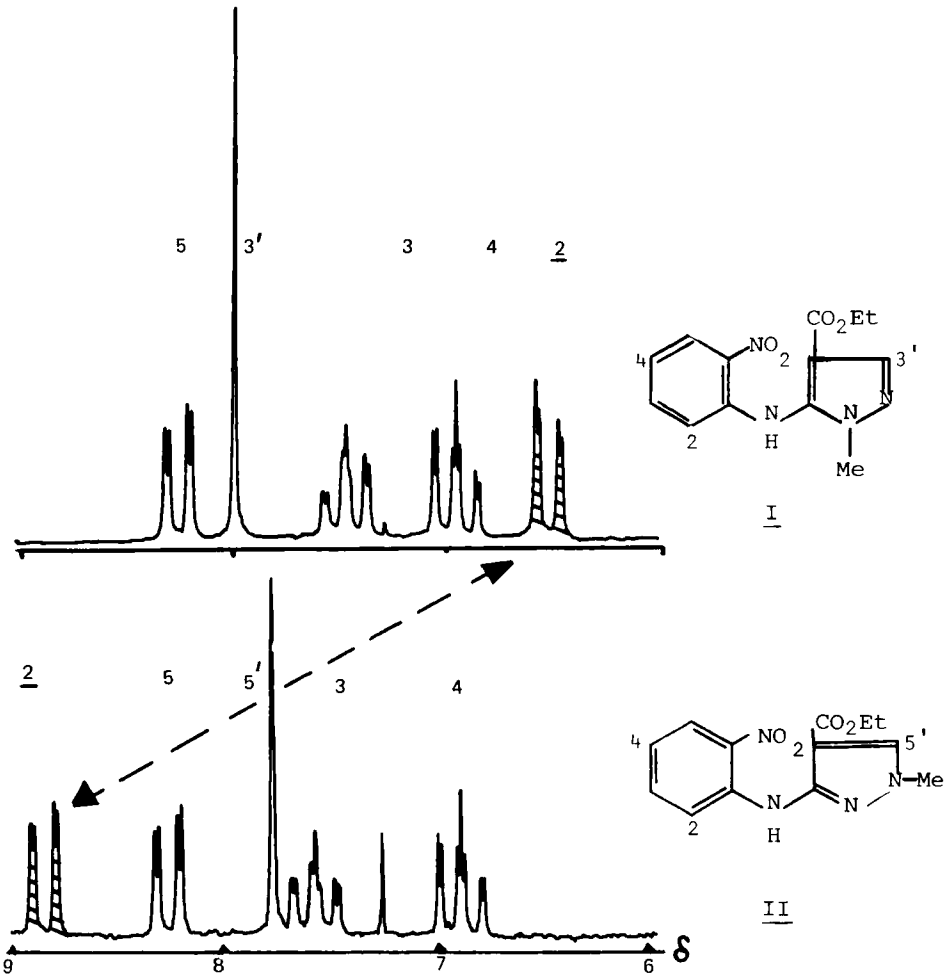

Figure 1. 80 MHz ^1H NMR Spectra of I and II (6-9δ)

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

This shifted signal was confirmed as H_2 by examination

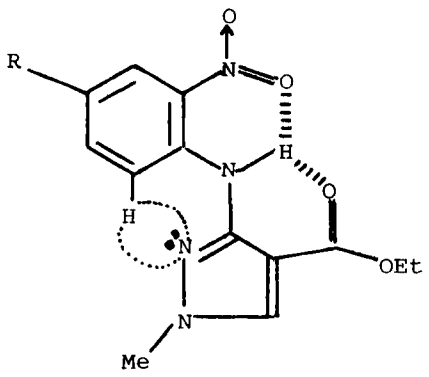

Figure 2

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 δ 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 ($CHCl_3$ solution) and Ultraviolet (MeOH solution) spectral data for isomeric pyrazoles I and II.

INFRARED (cm^{-1})	I	II
ν(C=O)	1715	1695
ν(N-H)	3345	3320
ULTRAVIOLET (nm)		
λ max	394	432

N-phenylpyrazole than those of N-phenylpyrrole[2,3] but the effect is very much smaller (0.3 δ).

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[4] 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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Received: January 3, 1980
Accepted: January 21, 1980