

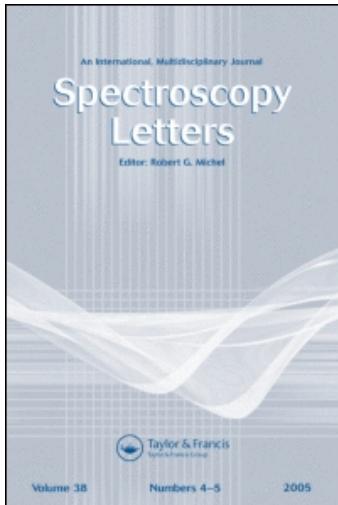
This article was downloaded by:

On: 30 January 2011

Access details: Access Details: Free Access

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## 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

David M. Rackham<sup>a</sup>; Sarah E. Morgan<sup>a</sup>; Jiban K. Chabrabarti<sup>a</sup>; Terrence M. Hotten<sup>a</sup>

<sup>a</sup> Lilly Research Centre Ltd., Surrey, England

**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>

## PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ANOMALOUS PROTON NMR DESHIELDING  
IN ANILINOPYRAZOLES

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

David M. Rackham\*, Sarah E. Morgan,  
Jiban K. Chabrabarti and Terrence M. Hotten.

Lilly Research Centre Ltd.  
Erl Wood Manor,  
Windlesham, Surrey,  
GU206PH, England.

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  $-\text{NH}-$  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

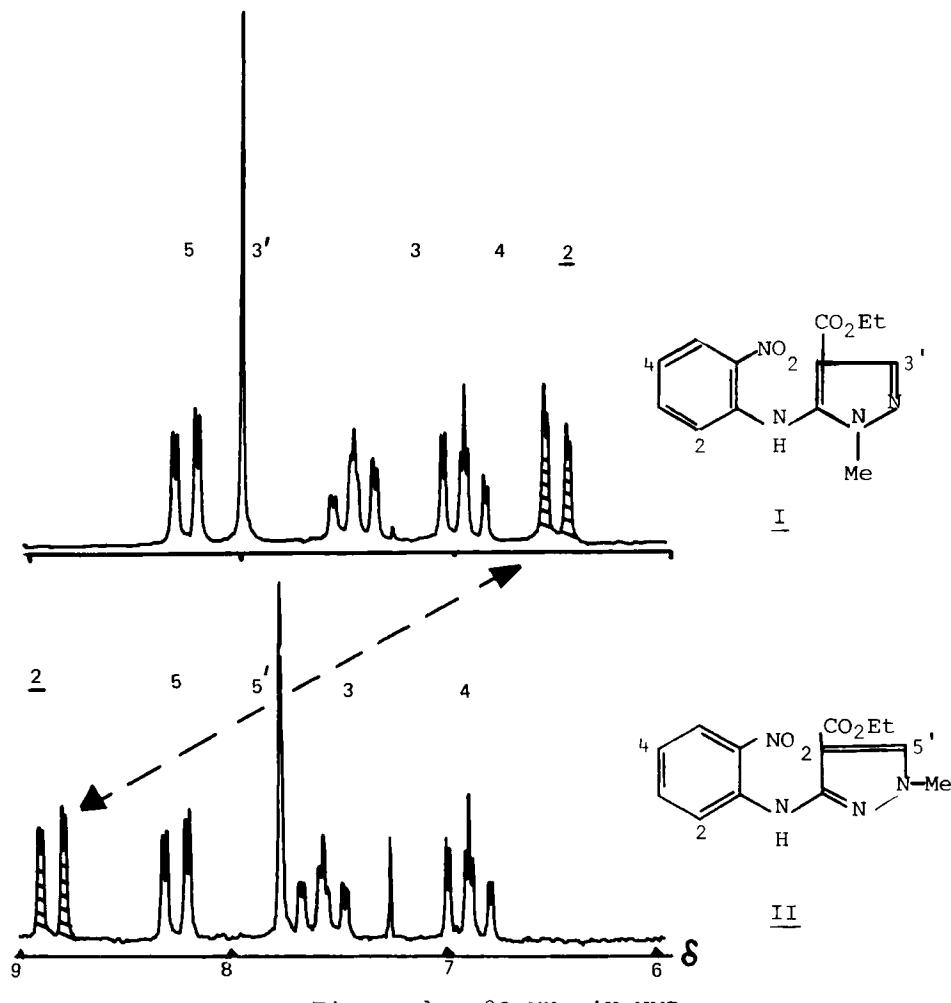


Figure 1. 80 MHz  $^1\text{H}$  NMR

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

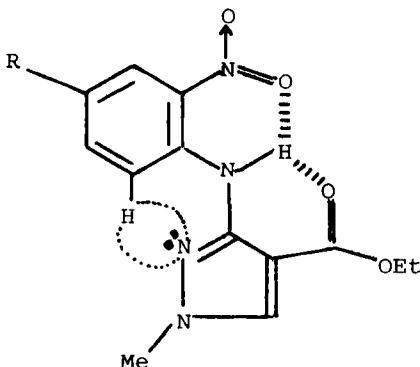


Figure 2

Hydrogen bonding in II

II, R = H

of the 4-chloro derivative (II below, R = Cl) in which H<sub>2</sub> 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<sub>2</sub> 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<sub>3</sub> solution) and Ultraviolet (MeOH solution) spectral data for isomeric pyrazoles I and II.

INFRARED (cm <sup>-1</sup> )	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<sup>2,3</sup> 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<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).

#### REFERENCES

1. J.K. Chakrabarti, T.A. Hicks, T.M. Hotten and D.E. Tupper, J. Chem. Soc. Perkin I, 937 (1978); Brit. Patent Appln. No. 7935846/1979.

2. I.L. Finar and D.M. Rackham, J. Chem. Soc. (B), 211, (1968).
3. J.N. Murrell, V.M.S. Gil and F.B. Van Duijneveldt, Rec. Trav. chim. 84, 1399, (1965).  
L.J. Bellamy, 'The Infrared Spectra of Complex Molecules', 3rd Edn., Wiley, New York, 1975, p.284.

Received: January 3, 1980  
Accepted: January 21, 1980