

The geometric configuration determination of 2-(1-aryl-1-oxopropan-2-ylidene)hydrazinecarboxamides with ^1H - ^1H NOESY

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We have shown that arylnitropropenones react with phenylhydrazine or hydrazide of benzoic acid to form *aza*-Michael adducts [1], which, under the influence of a base, transforms into 2-(1-aryl-1-oxopropan-2-ylidene)hydrazinecarboxamides **1-4**. They can exist as *E*- and *Z*-isomers as well as *s*-cis and *s*-trans conformers. The presence of a single set of signals in the ^1H and ^{13}C NMR spectra of compounds **1-4** indicates their configurational homogeneity (Fig. 1).

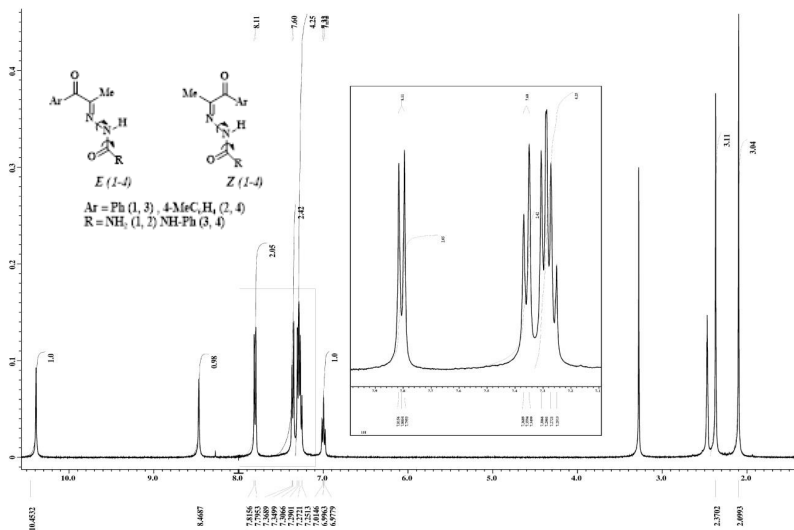


Figure 1. ^1H NMR spectrum of compound **4** ($\text{DMSO}-d_6$)

The aim of this study is to determine the geometric configuration of 2-(1-aryl-1-oxopropan-2-ylidene)hydrazinecarboxamides **1-4** using NMR spectroscopy, specifically employing the ^1H - ^1H NOESY experiment.

Studying compound **4** with ^1H - ^1H NOESY experiment revealed that the protons of the methyl and amide groups display the Overhauser nuclear effect, indicating an *E*-configuration of the $\text{C}=\text{N}$ bond (Fig. 2). Furthermore, the absence of a cross peak between the *o*-protons of the tolyl ring and the methyl group protons suggests an *s*-*trans* configuration for the $\text{C}=\text{N}$ and $\text{C}=\text{O}$ bonds.

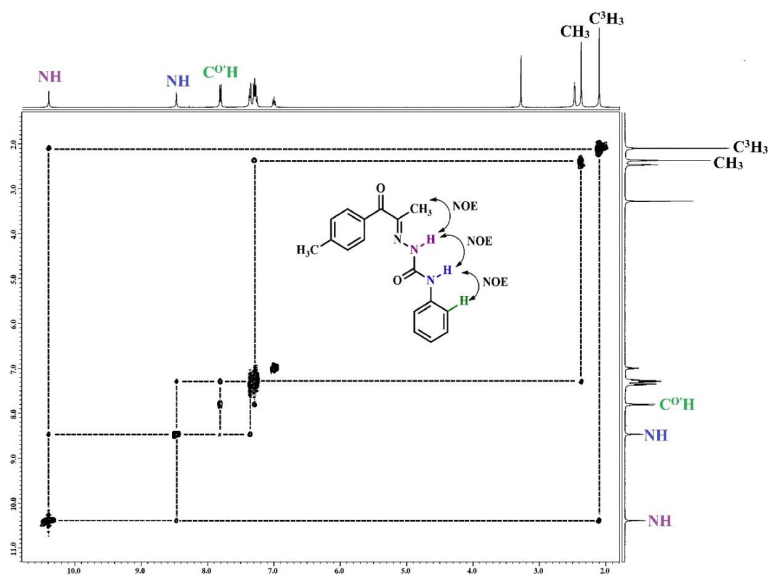


Figure 2. ^1H - ^1H NOESY spectrum of compound 4 (DMSO- d_6)

Assumptions made about the *E-s-trans* geometric configuration of the synthesized hydrazinecarboxamides series are validated by the X-ray structural analysis, as illustrated by compound 1 (Fig. 3).

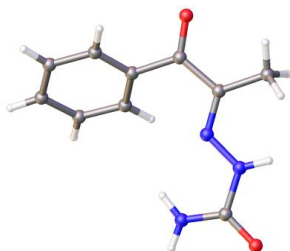


Figure 3. X-ray analysis of compound 1

Hence, the structure of (*2E*)-2-(1-aryl-1-oxopropan-2-ylidene)hydrazinecarboxamides has been reliably confirmed through the results of the ^1H - ^1H NOESY experiment and further supported by X-ray structural analysis

References

1. Adyukov I.S., Pelipko V.V., Makarenko S.V. 1-Aryl-3-nitroprop-2-en-1-ones in reactions with substituted hydrazines // Book of abstracts Conference "New Emerging Trends in Chemistry (NewTrendsChem-2023)". Yerevan (Armenia), 24-28 September 2023. P. 98.