

Nuclear Overhauser effect in determination the geometric configuration of the *N'*-substituted hydrazone methylpyruvate

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Alkyl 3-nitroacrylates are highly active substrates in the *aza*-Michael reaction [1-3]. This opens up perspectives for the preparation of original *N'*-substituted hydrazones of alkylpyruvates **1** [4].

The possibility of existence of compounds **1** in the form of *E*- or *Z*-isomers (C=N bond) and *s-cis*- or *s-trans*-conformational isomers [=N-NH, C(O)-NH, C(O)-R] makes them attractive structures for studying by 1D and 2D NMR spectroscopy methods.

The aim of this work was to study the fine structure of methyl 2-[2-(furan-2-ylcarbonyl)hydrazinylidene]propanoate **2** (Alk = Me, R = furan-2-yl) by NMR spectroscopy including the ¹H-¹H NOESY experiment.

The presence of one set of signals in the ¹H and ¹³C NMR spectra indicates the existence of hydrazinylidene propanoate **2** as the one configurational isomer (for all the bonds under consideration) in the DMSO-*d*₆ (Fig. 1).

At the same time, the signals at 6.68-7.95 ppm attract attention, one of which (δ_H 7.60 ppm) appears as a broadened singlet and makes the assignment of the signals of the furan ring protons not so unambiguous (Fig. 1).

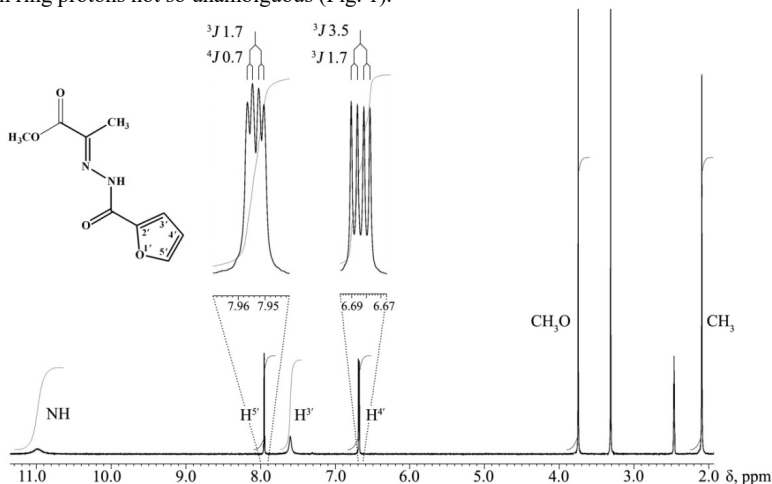


Figure 1. ¹H NMR spectrum of compound **2** (DMSO-*d*₆)

According to ^1H - ^1H NOESY experiments obtained with varying mix. time, the NOE correlation [5] in the spectra of compound **2** is demonstrated by the protons of the CH_3 and NH groups, indicating their close position in space, and, consequently, the existence of this compound in a $\text{DMSO-}d_6$ solution in the form of the *E*-isomer (Fig. 2). In addition, the signal of the proton of the NH group forms a cross-peak with the signal at δ_{H} 7.60 ppm, which allows the latter to be attributed to the proton C^3H . The correlations in the ^1H - ^1H NOESY spectrum allows one to assign the *s-trans*-configuration to the $=\text{N-NH}$, C(O)-Fur fragments and the *s-cis*-configuration to the C(O)-NH fragment. An additional confirmation of the *s-cis*-configuration of the C(O)-NH bond is the signal of the C(O) atom at 158 ppm in the ^{13}C NMR spectrum of compound **2**, which is in agreement with the literature data [6-8].

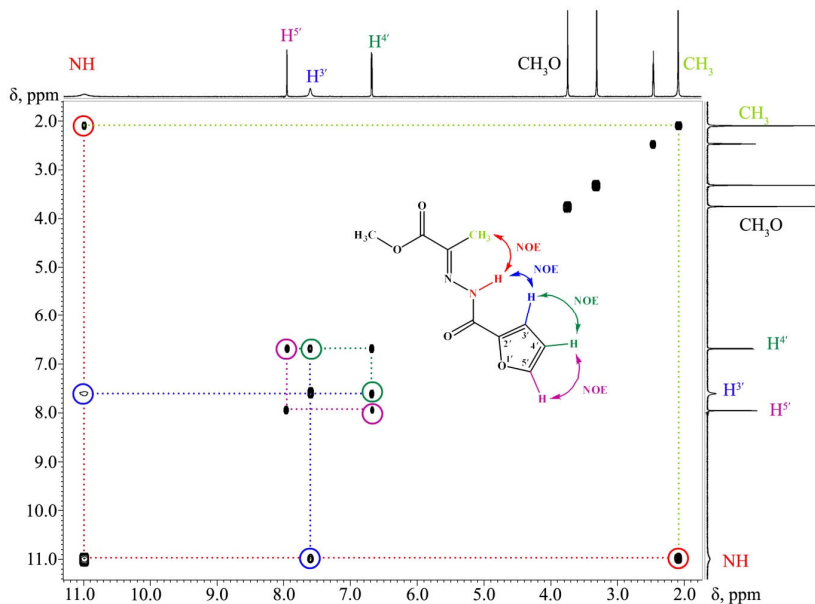
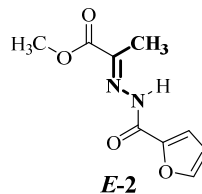


Figure 2. ^1H - ^1H NOESY spectrum of compound **2** ($\text{DMSO-}d_6$)

At the same time, the spectrum of ^1H - ^1H NOESY exhibits cross-peaks of the signal of the proton C^3H and the singlet at δ_{H} 6.68 ppm, making it possible to determine its belonging to the proton C^4H , while the cross-peak of this signal and the singlet at δ_{H} 7.95 ppm confirms the belonging of the latter to the proton C^5H (Fig. 2).

Signal assignment based on the ^1H - ^1H NOESY spectrum is consistent with the results of ^1H - ^1H dqf-COSY experiments obtained for compound **2** (Fig. 3).

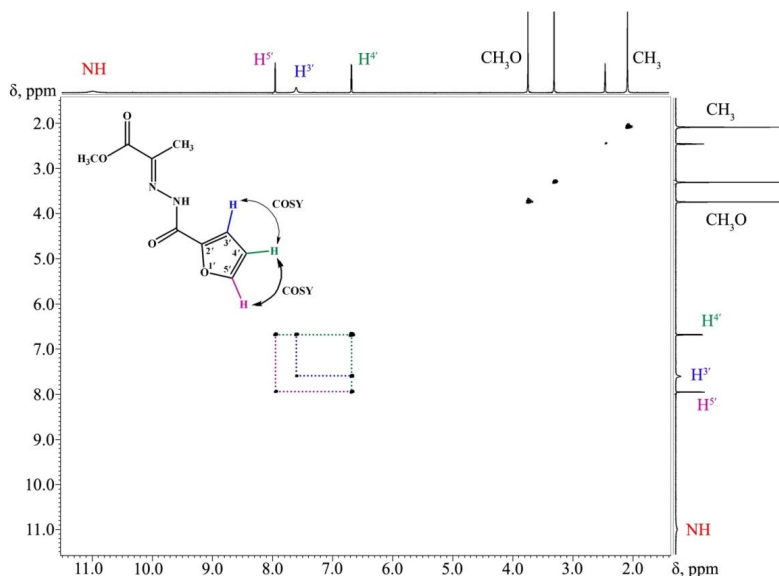


Figure 3. ^1H - ^1H dqf-COSY spectrum of compound **2** ($\text{DMSO}-d_6$)

Thus, the fine structure of hydrazinylidene propanoate **2** was determined by ^1H - ^1H NOESY experiment, the *Z*-configuration of the $\text{C}=\text{N}$ fragment was established, as well as the *s-trans*-configuration of the $=\text{N}-\text{NH}$, $\text{C}(\text{O})-\text{Fur}$ fragments, and the *s-cis*-configuration of the $\text{C}(\text{O})-\text{NH}$ fragment.

The studies were carried out in the center of collective use at the Faculty of Chemistry of the Herzen State Pedagogical University of Russia on the Jeol ECX-400A spectrometer at 399.78 (^1H) and 100.53 (^{13}C) MHz with standard experimental settings. The residual signals of a non-deuterated solvent (for ^1H nuclei) or the signals of a deuterated solvent (for ^{13}C nuclei) were used as a standard.

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