

Homo- and heteronuclear experiments of NMR spectroscopy in the structural study of polysubstituted furans

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Previously, it was shown that the reactions of alkyl 3-bromo-3-nitroacrylates with representatives of cyclic CH-acids lead to the synthesis of benzofurancarboxylates [1]. As a result of studying the interaction of alkyl 3-bromo-3-nitroacrylates with acyclic CH-acids (pentane-2,4-dione, methyl- and ethyl 3-oxobutanoates), we obtained polysubstituted furans **1-6**.

The aim of this work was to study the structure of such furans **1-6** by ^1H , ^{13}C NMR spectroscopy, including homo- (^1H - ^1H COSY) and heterocorrelation (^1H - ^{13}C HMQC, HMBC) experiments.

A structural feature of the substances **1-6** is the presence in their molecule of vicinal protons C^2H , C^3H , which form an *AMX*-type spin system with the protons of the methyl group at C^5 in the ^1H NMR spectra.

Thus, in the ^1H NMR spectrum of compound **4**, the C^2H proton resonated as a doublet at 6.12 ppm (3J 2.0 Hz), the C^3H proton resonated as a multiplet at 4.36-4.39 ppm, and the protons of the methyl group at C^5 formed a doublet at 2.41 ppm (3J 1.4 Hz) (Fig. 1).

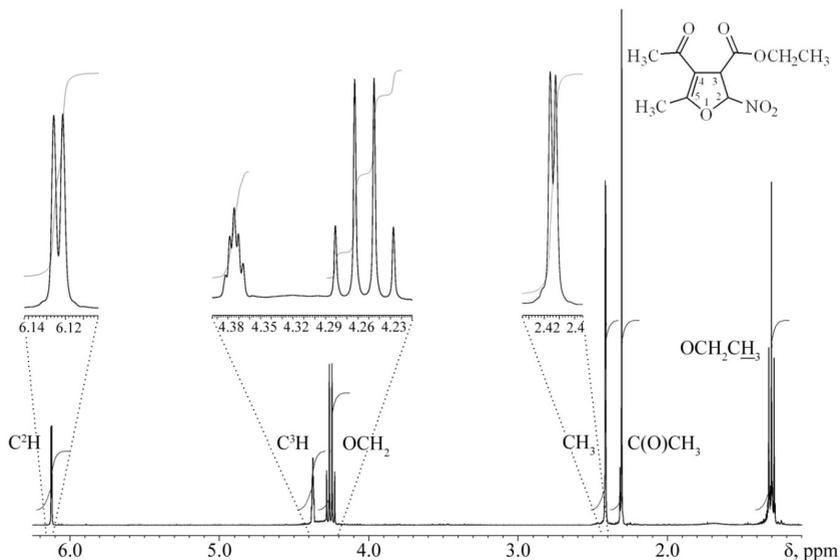
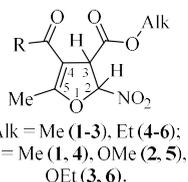


Figure 1. ^1H NMR spectrum of compound **4** (CDCl_3)

The assignment of signals is confirmed by the results of ^1H - ^1H dqf-COSY experiments obtained for compound **4** (Fig. 2).

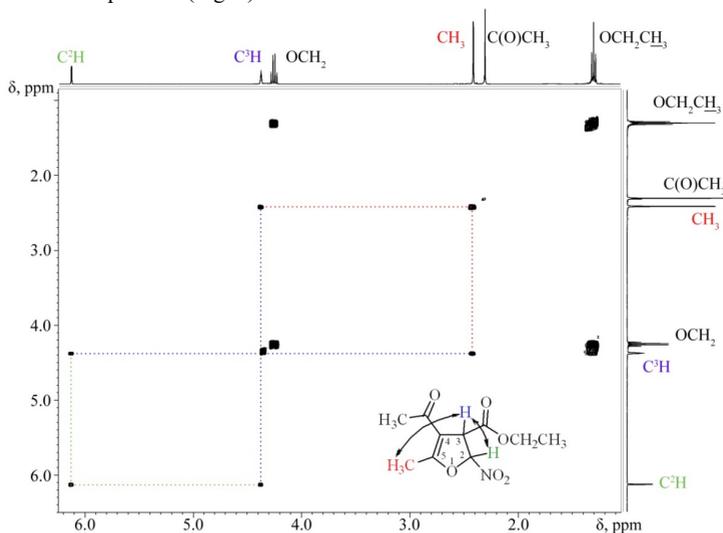


Figure 2. ^1H - ^1H dqf-COSY spectrum of compound **4** (CDCl_3)

^{13}C - $\{^1\text{H}\}$ NMR spectra of furans **1-6** contain signals of all structural fragments. At the same time, the structural feature of the synthesized molecules is the presence of four quaternary carbon atoms (Fig. 3).

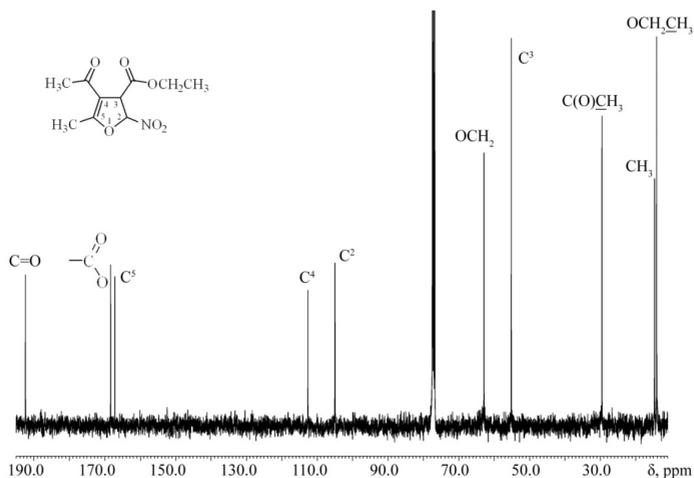


Figure 3. ^{13}C NMR spectrum of compound **4** (CDCl_3)

The assignment of signals in the ^{13}C - $\{^1\text{H}\}$ NMR spectra was based on the results of the ^1H - ^{13}C HMQC and ^1H - ^{13}C HMBC experiments.

Thus, in the ^1H - ^{13}C HMQC spectrum of compound **4**, the signal of C^2H proton (δ_{H} 6.12 ppm) forms a cross-peak with the carbon atom at δ_{C} 105.00 ppm, C^3H proton (δ_{H} 4.36-4.39 ppm) and carbon at δ_{C} 55.18 ppm, methyl group protons at C^5 (δ_{H} 2.41 ppm) and carbon at δ_{C} 14.69 ppm. The proton signals of the $\text{CH}_3\text{CH}_2\text{O}$ ester fragment (δ_{H} 1.30, 4.25 ppm) form cross peaks with carbon atoms at δ_{C} 14.10 ppm and δ_{C} 62.89 ppm, respectively. The signal of the methyl protons of the acetyl fragment (δ_{H} 2.31 ppm) forms a cross peak with the signal of the carbon atom at δ_{C} 29.55 ppm (Fig. 4).

The assignment of the signals of quaternary carbon atoms was based on the results of the ^1H - ^{13}C HMBC experiment. The spectrum of compound **4** (Fig. 5) shows cross peaks of the signal of the methylene protons CH_2O (δ_{H} 4.25 ppm) and the carbon atom at δ_{C} 168.35 ppm ($\text{O}-\text{C}=\text{O}$), methyl protons of the acetyl fragment (δ_{H} 2.31 ppm), and carbon atoms at δ_{C} 112.60 ppm (C^4) and δ_{C} 192.41 ppm ($\text{C}=\text{O}$), as well as cross peaks of protons of the methyl group C^5 (δ_{H} 2.41 ppm)/ C^5 (δ_{C} 167.18 ppm).

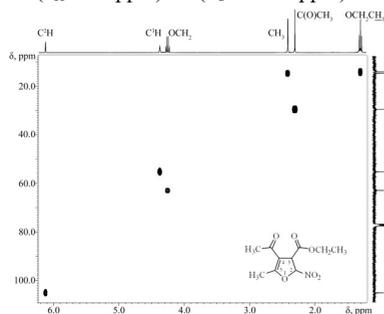


Figure 4. ^1H - ^{13}C HMQC spectrum of compound **4** (CDCl_3)

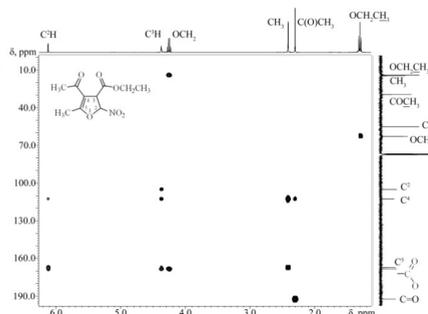


Figure 5. ^1H - ^{13}C HMBC spectrum of compound **4** (CDCl_3)

Thus, the study of polysubstituted furans using a complex of homo- and heterocorrelation experiments of NMR spectroscopy makes it possible to completely describe their structure and to assign the signals of ^1H , ^{13}C atoms of all fragments of the molecule.

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 (13C) 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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References

1. Pelipko, V. V., Baichurin, R. I., Kondrashov, E. V., Makarenko, S. V. Russ. J. Gen. Chem. 2021, 91, 167.