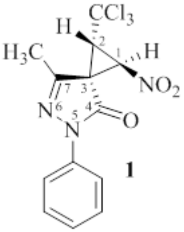
Configuration Determination of Regioisomeric Spirocyclopropanes Using NMR Spectroscopy Methods

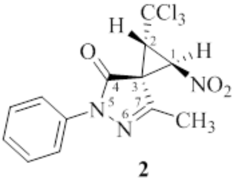
Pelipko V.V., Pilipenko I.A., Baichurin R.I., Makarenko S.V.
Herzen State Pedagogical University of Russia, Department of Organic Chemistry, Laboratory of Nitrocompounds, Center of collective use at the Faculty of Chemistry "Instrumental methods for the study of nitro compounds, coordination, biologically active substances and nanostructured substances" 48 Moyka River Embankment, Saint Petersburg 191186, Russia
E-mail: kohrgpu@yandex.ru
http://kohrgpu.ru, http://ckpo.herzen.spb.ru/?page=organic-chemistry

The study of the interaction of 1-bromo-1-nitro-3,3,3-trichloropropene with phenylmethylpyrazolone showed that the reaction leads to the formation of two regioisomeric spiro-fused nitrocyclopropanes **1**, **2**, similarly to the reactions of bromonitroacrylates [1]. The products can be separated by silica gel column chromatography. The isolated regioisomers **1**, **2** are very attractive objects for studying the structure by 1D and 2D NMR spectroscopy experiments due to their rigidly fixed structure.

In the ^{13}C NMR spectra the signals of C^2 atom appear at 52.8–56.0 ppm in the form of doublets with a characteristic *J*-coupling constants $^1JC^2\text{-}H^2$ = 169.7–172.7 Hz, and the signals of C^1 atom appear at 69.6–72.4 ppm in the form of doublet-doublets with constants $^1JC^1\text{-}H^1$ = 189.7–194.0 and $^2JC^1\text{-}H^2$ = 4.0–4.9 Hz (Fig. 1), which confirms their cyclopropane nature [2, 3, 4]. The observed in the ^{1}H NMR spectra of compounds **1**, **2** *J*-coupling constants of the methine protons of the cyclopropane ring ($^3JH^1\text{-}H^2$ = 6.6-6.8 Hz) indicates their *trans* configuration (Fig. 2).



1



2

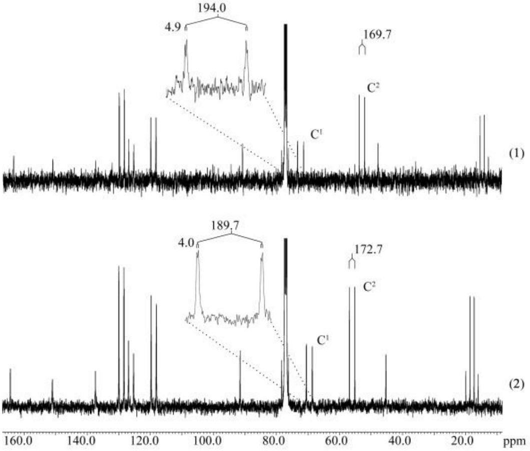


*Figure 1. ^{13}C NMR spectrum of spectrum of compounds **1, 2**(CDCl$_3$)*

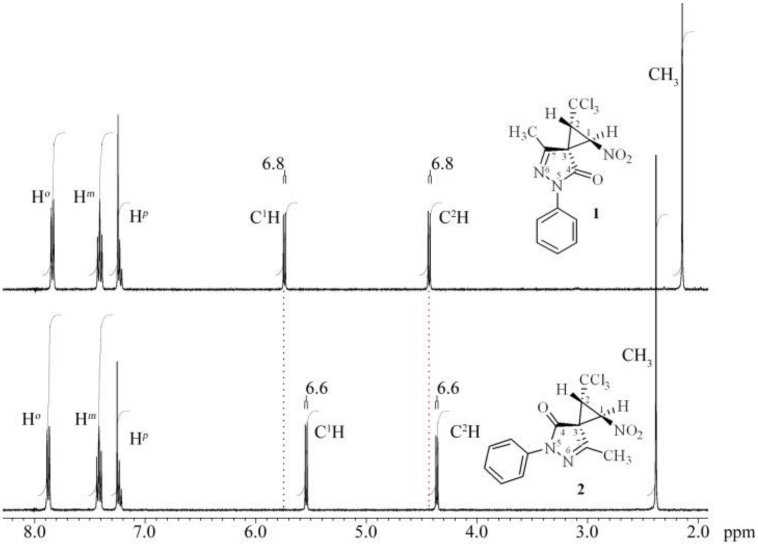


Figure 2. ^1H NMR spectrum of compounds **1, 2**($CDCl_3$)

In turn, the results of 1H-1H NOESY experiments for individual diastereomers obtained with a variable value of mix. time (τ 0.5, 1, 1.5, 2 sec) show NOE correlations of C2H/CH_3 (heterocycle) protons for diastereomer 1 and C1H/CH_3 (heterocycle) for diastereomer (Fig. 3, 4). The presence of these correlations indicates the realization for diastereomer 1 of such an arrangement of spirocycles, in which the methyl group of pyrazolone and the nitro groups are on the same side of the cyclopropane ring, while for diastereomer 2, this position is occupied by the methyl and trichloromethyl groups.

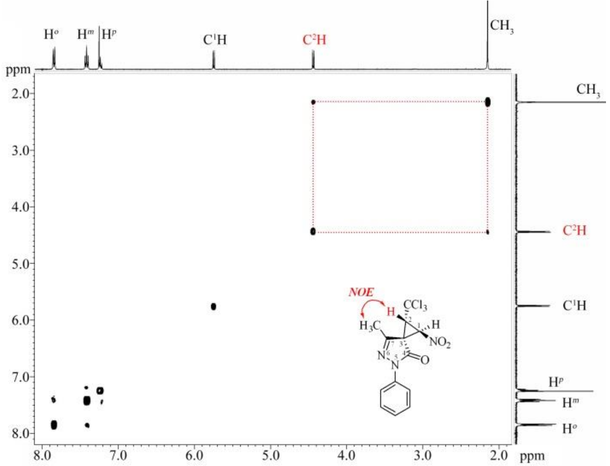


Figure 3. ^1H-^1H NOESY spectrum of compound **1** ($CDCl_3$)

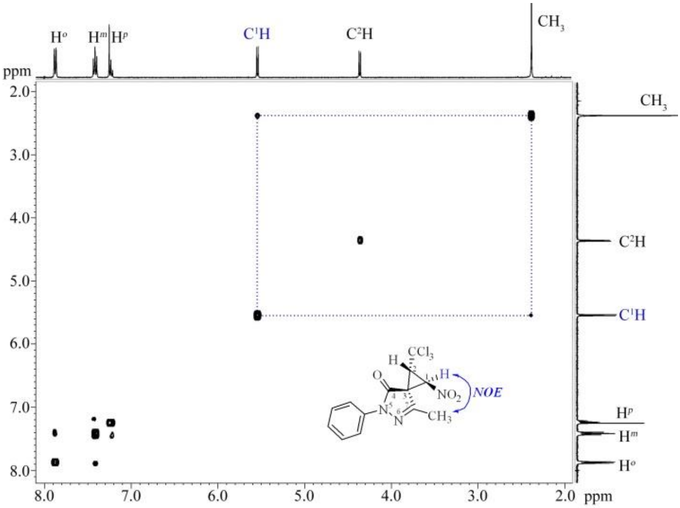


Figure 4. ^1H-^1H *NOESY spectrum of compound* **2** *(*$CDCl_3$*)*

Thus, the study of compounds **1**, **2** using 1D and 2D NMR spectroscopy experiments made it possible to establish the fine structure of the obtained regioisomeric spirocyclopropanes.

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 (Royal Probe) 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.*

References

1. M.M. Pavchenko, V.V. Pelipko, K.A. Lyssenko, S.V. Makarenko, R.I. Baichurin. *In Magnetic resonance and its applications. Spinus-2018*, 221-222 (2018).
2. V.V. Pelipko, R.I. Baichurin, S.V. Makarenko. *In Magnetic Resonance and its Applications*, 230-231 (2020).
3. A.J. Gordon, R.A. Ford. The Chemist's Companion. New York: Wiley, 1972.
4. R. Silverstein, F. Webster, D. Kimle. Spectrometric Identification of Organic Compounds: BINOM. Laboratoriya Znanii. Moscow, 2012.