

Solution to bridged bicyclic molecule NMR challenge

Andrii V. Kozytskyi^{1,2} · Andrii V. Bondarenko^{1,2}

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The winner of the Bridged bicyclic molecule NMR challenge (published in volume 415 issue 24) is:

Mirsadra Molaei, Department of Pharmaceutical Chemistry, Semmelweis University, Budapest, Hungary.

The award entitles the winner to select a Springer book of their choice up to a value of €100,-.

Our Congratulations!

The Bridged bicyclic molecule NMR Challenge asked readers to identify isomers of bicyclo[2.2.1]alkane from the ¹H-NMR spectrum [1]. The most deshielded protons with signals in the vicinity of 4.5 ppm are from protons located at the base of the bridge. The key difference between the two spectra is that one of them shows two triplets, while the other shows a triplet and a doublet (Fig. 1).

At this point, one has to remember the Karplus equation that describes the variation of the coupling constants between two hydrogen atoms as a function of the dihedral angle between them [2]. The magnitude of this coupling is generally smallest when the torsion angle is close to 90° and largest at angles of 0 and 180° (Fig. 2).

Figure 2 illustrates the dihedral angles between the epoxy bridge hydrogen atoms and their neighboring hydrogen atoms in *endo*- and *exo*-isomers. Hence, according to the Karplus equation, in the case of the *endo*-isomer, the proton at the base of the bridge (closer to CH₂OH) position has more complex multiplicity than in the *exo*-isomer, as illustrated in Fig. 3.

Keeping this in mind, let us analyze the ¹H-NMR spectra of these isomers (Fig. 1). So, as can be seen from Fig. 1, in the *endo*-isomer of the bicyclo[2.2.1]alkane, both ¹H signals

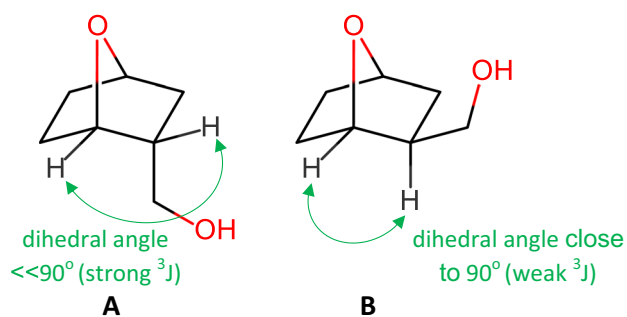


Fig. 1 Dihedral angles between the hydrogen atoms and their neighbors in *endo*- isomers (A) and *exo*- isomers (B)

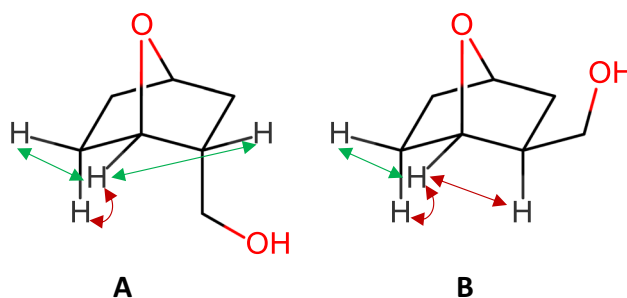


Fig. 2 Illustration of strong (green arrows) and weak (red arrows) spin-couplings for the protons at the base of the bridge in *endo*- isomers (A) and *exo*- isomers (B)

of hydrogen atoms at the base of the bridge (4.4...4.6 ppm) will appear as triplets (A, Fig. 1, left spectrum). At the same time, for the *exo*-isomer, they appear as one triplet and one doublet (B, Fig. 1, right spectrum).

This article is the solution to the Analytical Challenge to be found at <https://doi.org/10.1007/s00216-023-04887-1>

✉ Andrii V. Kozytskyi
kozytskyi@ukr.net

¹ Taras Shevchenko National University of Kyiv,
Volodymyrska Str. 64, Kyiv 01601, Ukraine

² Enamine Ltd, Winston Churchill Str. 78, Kyiv 02094,
Ukraine

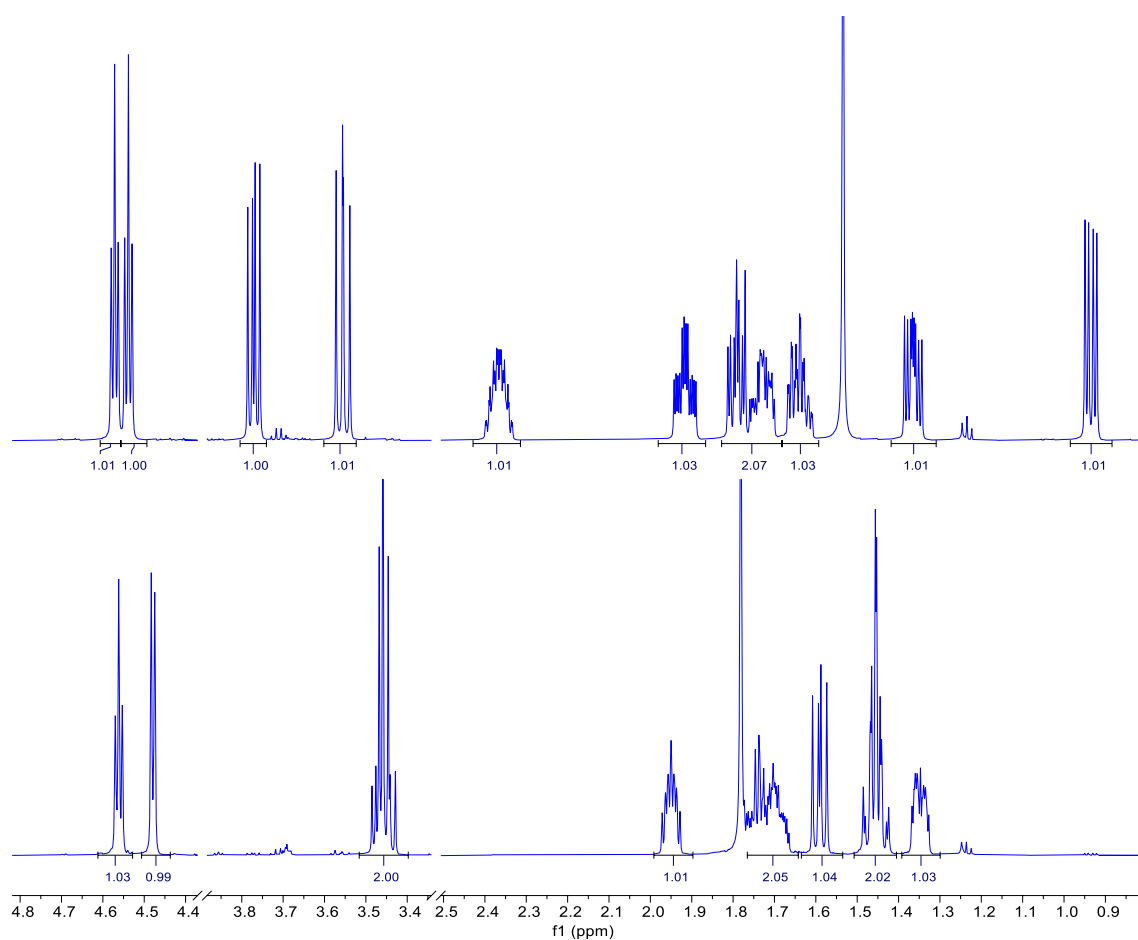


Fig. 3 Detail of $^1\text{H-NMR}$ spectra of *endo*- and *exo*- isomers of bicyclo[2.2.1]alkane in CDCl_3

Declarations

Conflict of interest The authors declare no competing interests.

2. Dalton L. Chem Eng News. 2003;81(51):37. <https://doi.org/10.1021/cen-v081n036.p037>.

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