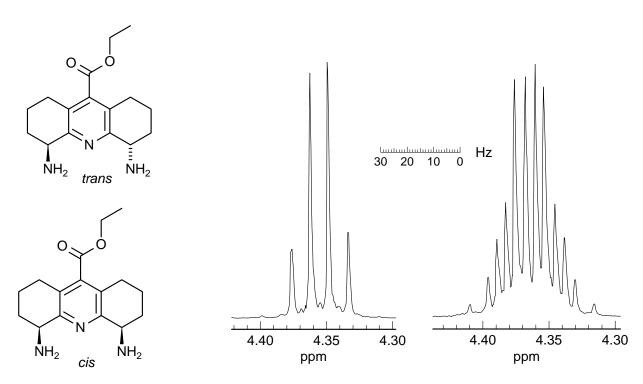
Problem R-08H (C₁₆H₂₃N₃O₂). Partial 500 MHz ¹H NMR spectrum of two isomers of a pyridyl diamine are shown below. Each signal integrates to 2 protons. These spectra were used by the researchers to assign stereochemistry. (Kneeland, D. M.; Ariga, K.; Lynch, V. M.; Huang, C.-Y.; Anslyn, E. V. *J. Am. Chem. Soc.* **1993**, *115*, 10042)

- (a) Assign the signal (circle the protons on the structures).
- (b) Explain the very different appearance of the signal in the two isomers. Do not attempt to do a numeric analysis, but provide sufficient detail to show that you understand the spectra. Identify which isomer corresponds to which spectrum, and explain (briefly) how you made the assignment.

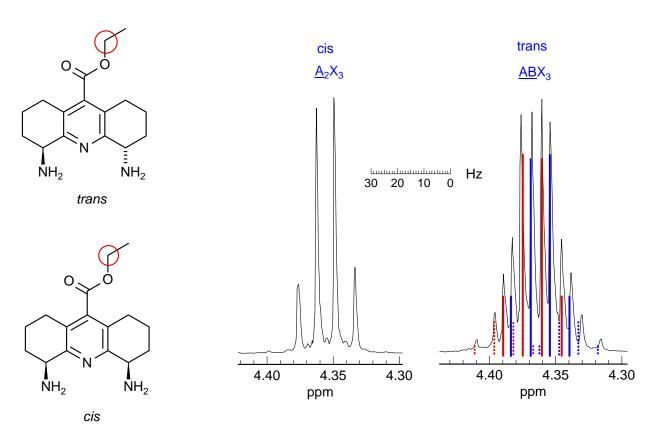


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4 O-CH₂ signal

(b) Explain the very different appearance of the signal in the two isomers. Do not attempt to do a numeric analysis, but provide sufficient detail to show that you understand the spectra. Identify which isomer corresponds to which spectrum, and explain (briefly) how you made the assignment.



The cis isomer has a plane of symmetry which bisects the ethyl group, hence the O-CH₂ is NOT diastereotopic (they are enantiotopic). Thus see a simple quartet.

The trans isomer is chiral, the CH₂ group is diastereotopic, and the ethyl group forms an ABX₃ pattern