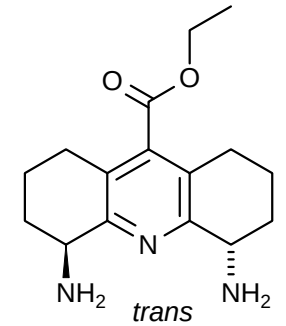
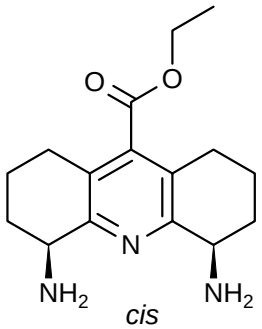
Problem R-08H ($C_{16}H_{23}N_3O_2$). Partial 500 MHz ^{1}H NMR spectrum of two isomers of a pyridyl diamine are shown below. Each signal integrates to 2 protons. These spectra were used by the researchers to assign stereochemistry. (Kneeland, D. M.; Ariga, K.; Lynch, V. M.; Huang, C.-Y.; Anslyn, E. V. *J. Am. Chem. Soc*. **1993**, *115*, 10042)

(a) Assign the signal (circle the protons on the structures).

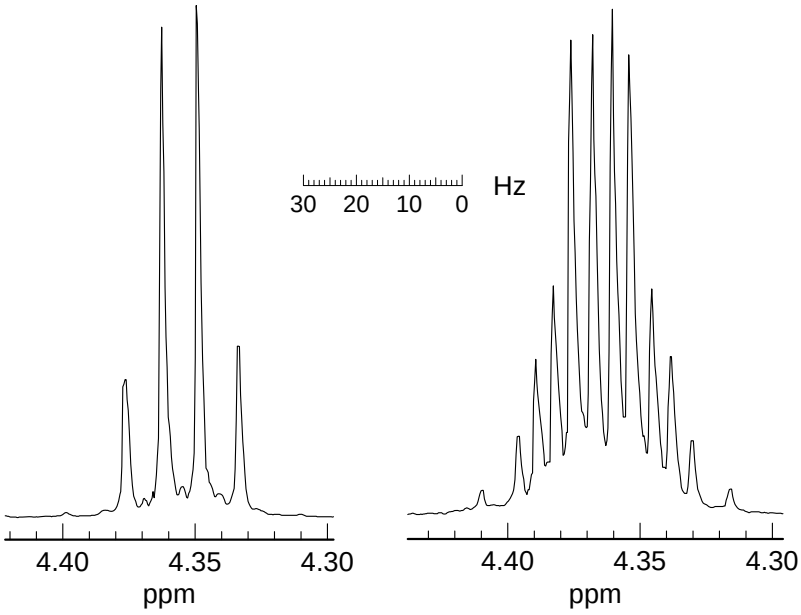
(b) Explain the very different appearance of the signal in the two isomers. Do not attempt to do a numeric analysis, but provide sufficient detail to show that you understand the spectra. Identify which isomer corresponds to which spectrum, and explain (briefly) how you made the assignment.



trans



cis



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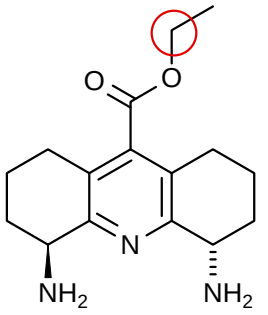
(a) Assign the signal (circle the protons on the structures).

4 O-CH_2 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.



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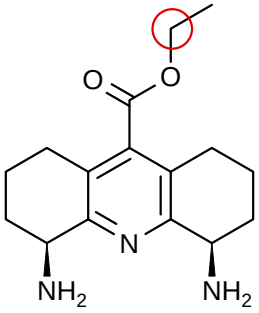
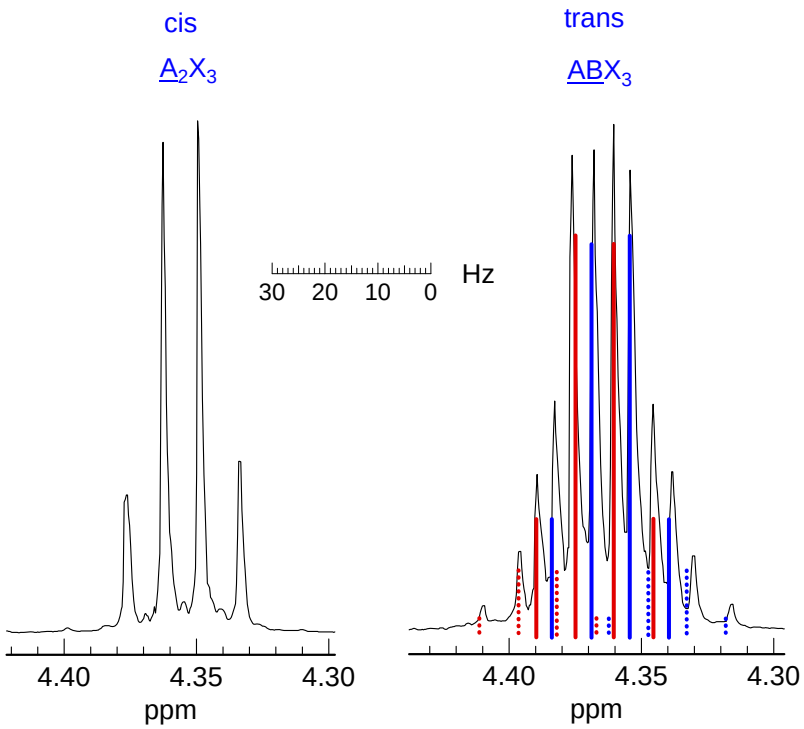


cis



6 The cis isomer has a plane of symmetry which bisects the ethyl group, hence the O-CH_2 is NOT diastereotopic (they are enantiotopic). Thus see a simple quartet.

The trans isomer is chiral, the CH_2 group is diastereotopic, and the ethyl group forms an ABX_3 pattern