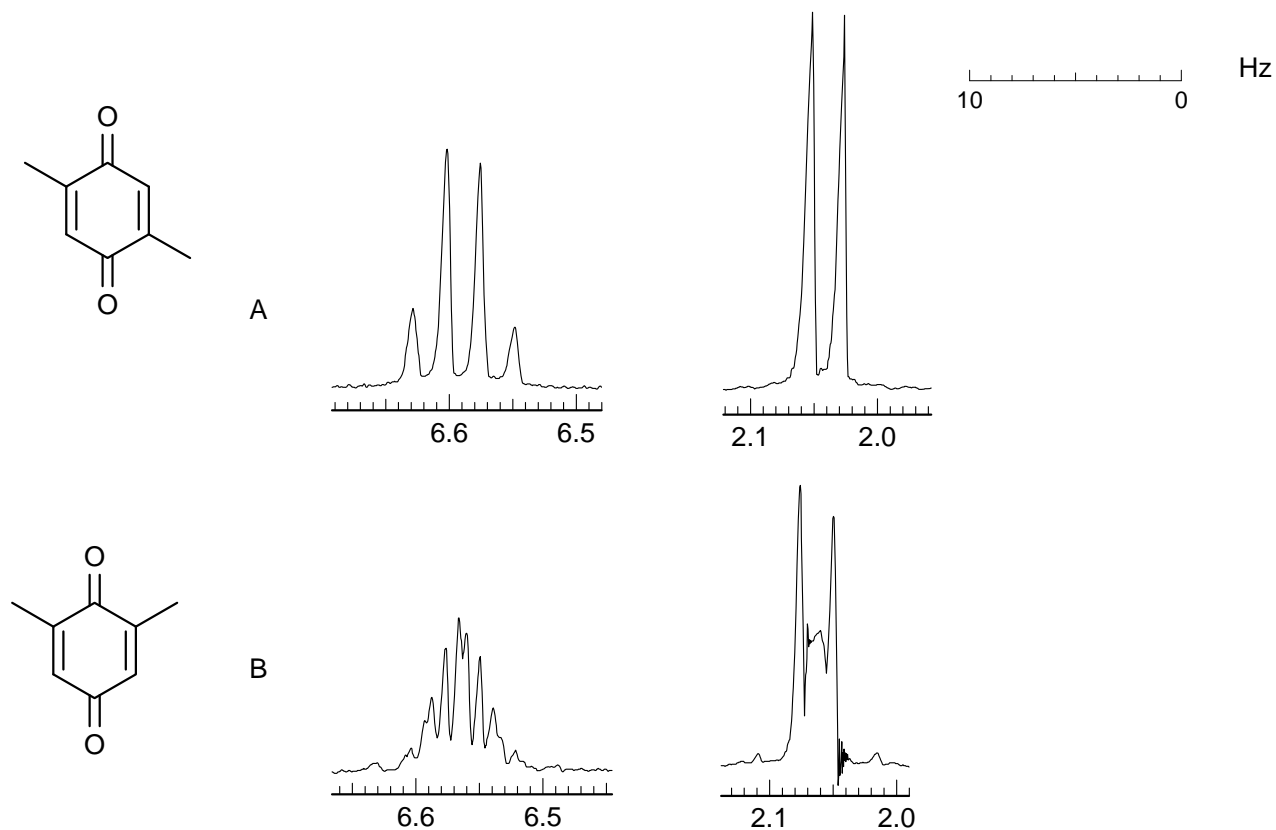


**Problem R-08F** ( $C_8H_8O_2$ ). Shown below are the 60 MHz  $^1H$  NMR spectra of two isomers of dimethylbenzoquinone (Becker, E. D. "High Resolution NMR, 2nd ed., Academic Press, 1980, p. 166).



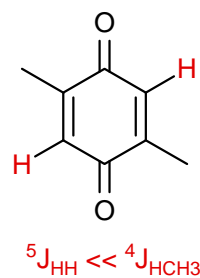
(a) What kind of patterns are these (e.g., ABMX)? \_\_\_\_\_

(b) Analyze the multiplets in spectrum A (interpret the coupling).

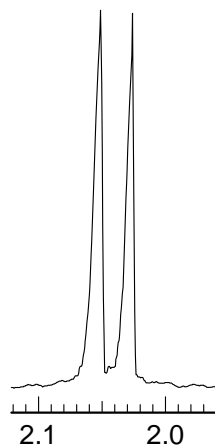
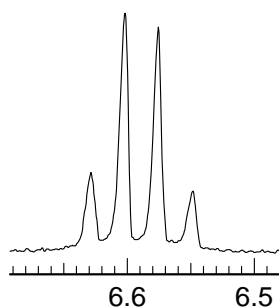
(c) Explain the origins of the very different appearance of the multiplets in spectrum B. Be specific and brief.

(d) Would you expect spectrum B to be more like A at 600 MHz? Explain.

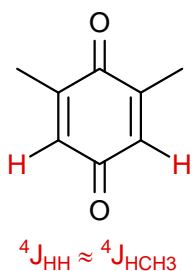
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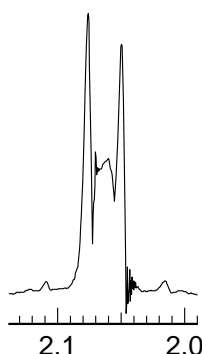
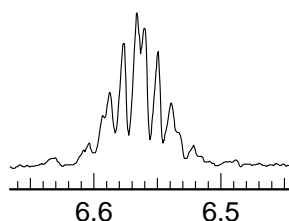
A



10 0 Hz



B



3 (a) What kind of patterns are these (e.g., ABMX)?  $A_3A_3'XX'$

(b) Analyze the multiplets in spectrum A (interpret the coupling).

$\delta$  2.04 d,  ${}^4J = 1.6$  Hz to vinyl proton

2  $\delta$  6.59 q,  ${}^4J = 1.6$  Hz to methyl group

This is normal 4-bond allylic coupling

(c) Explain the origins of the very different appearance of the multiplets in spectrum B. Be specific and brief.

6 In B the two vinyl protons are coupled to each other, with an expected  ${}^4J$  of 1.6 Hz ( ${}^4J \gg {}^5J$ ) and have zero chemical shift, so anything coupled to these protons such as the methyl group shows "virtual coupling" effects of the  $AA'XX'$  type.

In A the coupling between the vinyl protons is very small ( ${}^5J_{XX'} = 0$ ) so the two  $CH_3-C=C-H$  systems do not interact, and a simple  $A_3X$  system results (could be called  $(A_3X)_2$ ).

(d) Would you expect spectrum B to be more like A at 600 MHz? Explain.

4 No, these effects are field-independent - the  $\Delta\delta_{XX'}$  would be zero at any field, and spectrum B would look exactly the same at 600 MHz as it does at 60 MHz (assuming the instrument could be tuned as well - tuning measured in Hz)