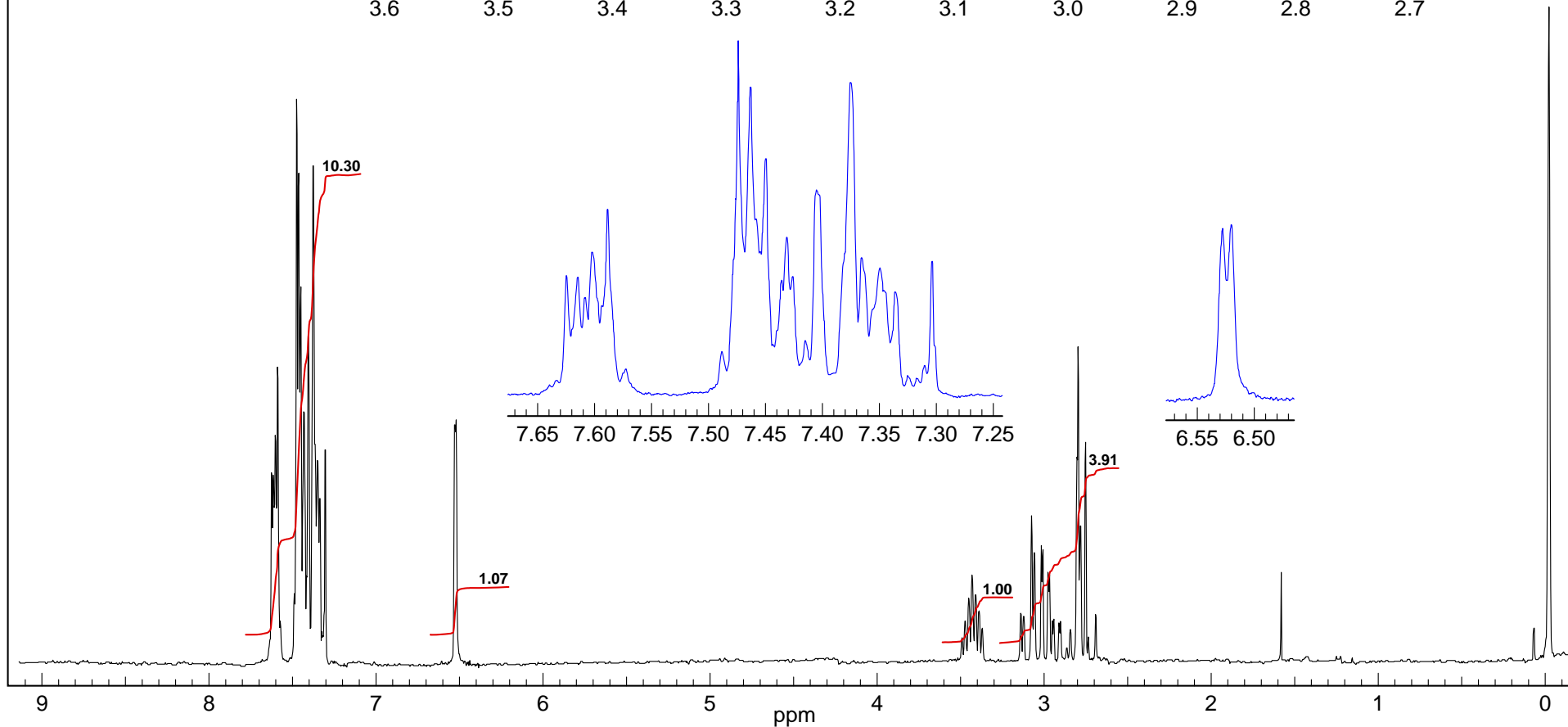
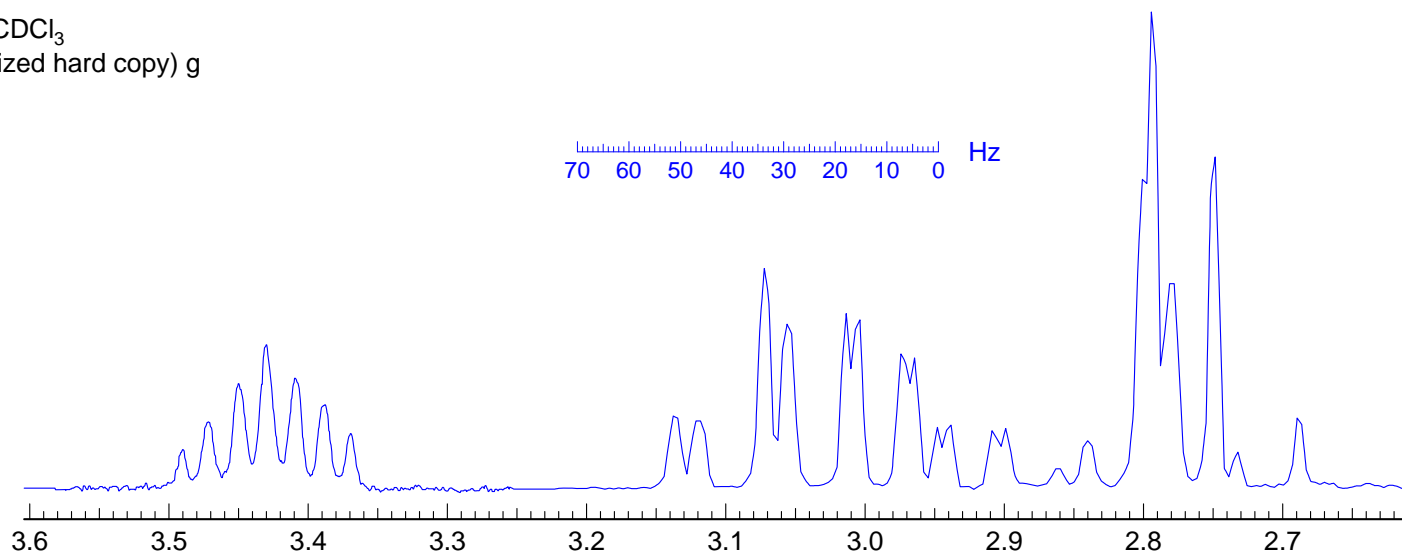
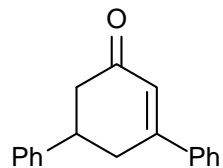


Problem R-07I (C₁₈H₁₆O)

270 MHz ¹H NMR spectrum in CDCl₃

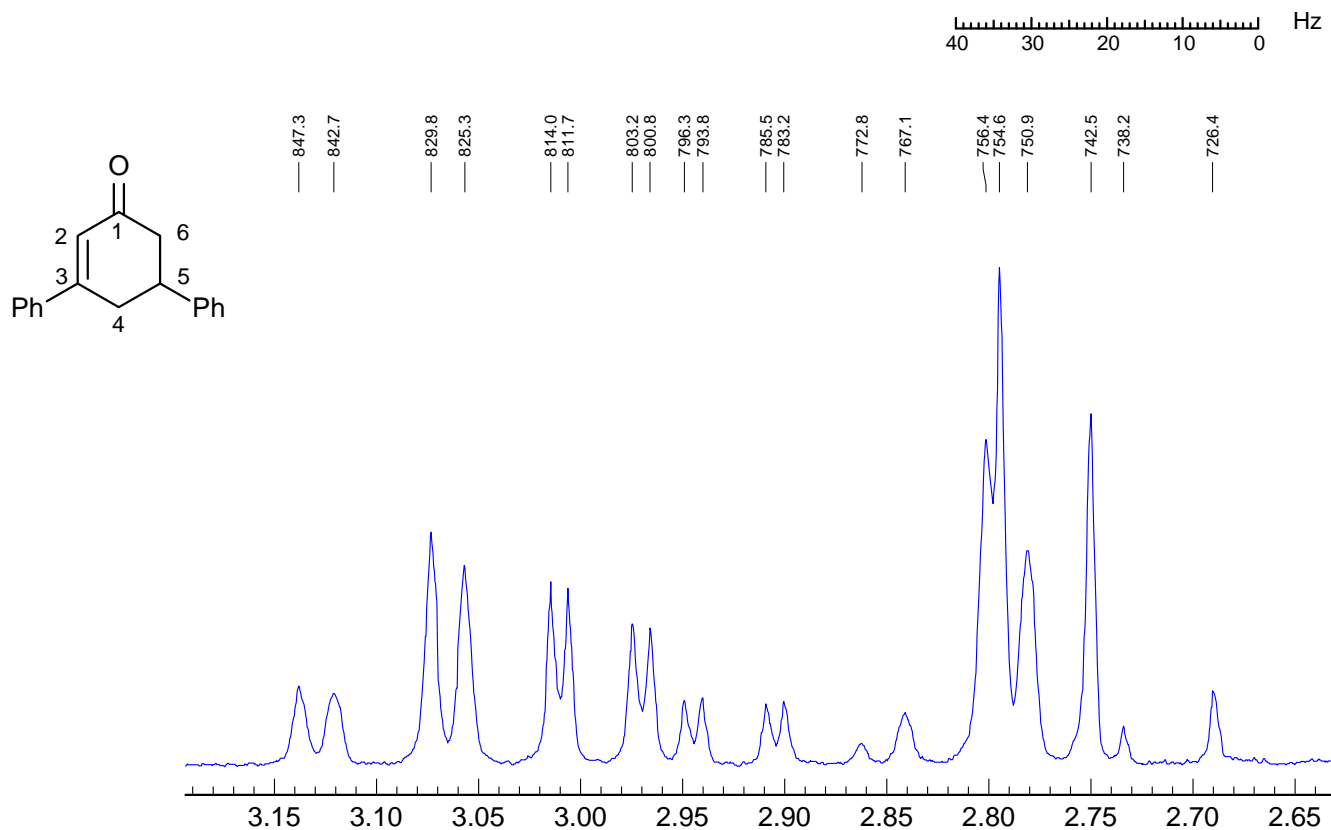
Source: Mike Bowe/Reich (digitized hard copy) g



Problem R-071. A proton NMR spectrum of 3,5-diphenylcyclohexenone is shown on the next page. This problem requires you to do an analysis of parts of the NMR spectrum.

(a) Explain the coupling in the peak at δ 6.5.

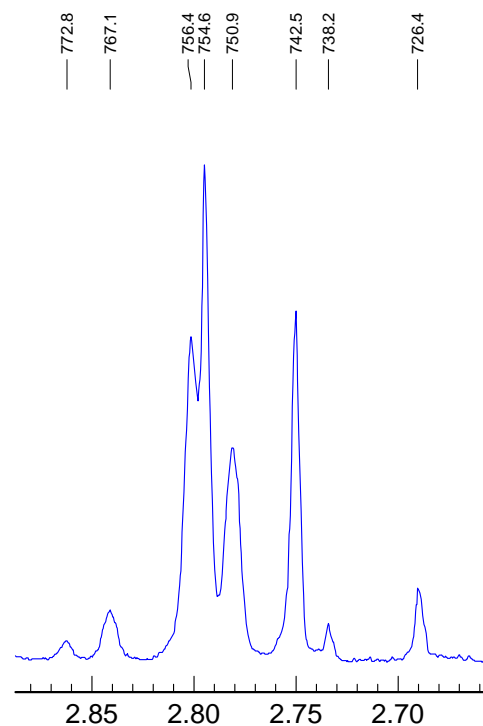
(b) Analyze the four-proton multiplet at δ 2.5-3.2. You may use first order ("AMX") analysis. Draw a coupling tree over the expansion below. Label each chemical shift position with a proton assignment (e.g., H-3ax or H-2eq). Give the values of coupling constants in the form $J_{3ax-2eq} = 1.2$ Hz.



(c) Explain why some of the peaks in the multiplet between δ 2.6 and 3.2 are broad, whereas others are sharp.

(d) Draw the conformation of the compound, labelled with δ values for each of the 6 non-phenyl protons.

(e) Below is a reproduction of the multiplet between δ 2.6 and δ 2.8. Analyze this multiplet as the AB part of an ABX pattern, using the peak positions (in Hz) shown. Calculate accurate coupling constants and chemical shifts. If there is more than one solution, present both. Show your work, and tabulate your data in an easily readable form.



(f) Since the X-part is complicated by additional coupling (it's really an ABMNXY pattern), suggest ways to distinguish between solutions 1 and 2?

30

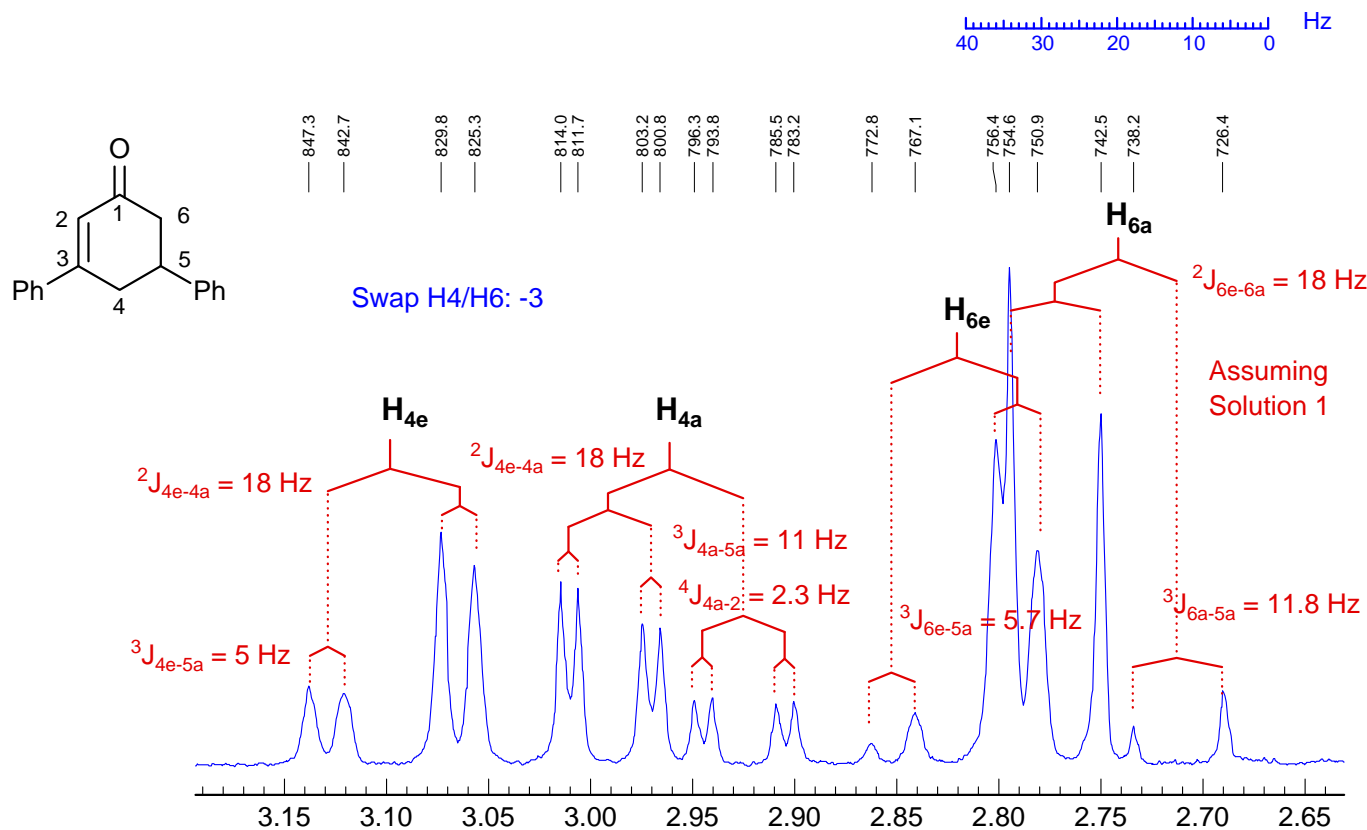
Problem R-071. A proton NMR spectrum of 3,5-diphenylcyclohexenone is shown on the next page. This problem requires you to do an analysis of parts of the NMR spectrum.

(a) Explain the coupling in the peak at δ 6.5.

3

This is the vinyl proton H-2, a doublet with $^4J_{2-4a} = 2$ Hz. Long range coupling is largest when the C-H bond is perpendicular to the π system. This coupling allows one make the distinction between the 2 and 6 protons. The H_{6a} proton shows no such coupling.

(b) Analyze the four-proton multiplet at δ 2.5-3.2. You may use first order ("AMX") analysis. Draw a coupling tree over the expansion below. Label each chemical shift position with a proton assignment (e.g., H-3ax or H-2eq). Give the values of coupling constants in the form $J_{3ax-2eq} = 1.2$ Hz.



7

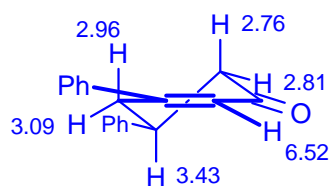
(c) Explain why some of the peaks in the multiplet between δ 2.6 and 3.2 are broad, whereas others are sharp.

2

The equatorial protons H_{4e} and H_{6e} are noticeably broader than the axial ones. This is presumably because there is a small coupling (4J) of the "W" type between them, and also between them and H₂.

(d) Draw the conformation of the compound, labelled with δ values for each of the 6 non-phenyl protons.

3



Look for correct 4/6 and ax/eq assignments either here or in part (b)

(e) Below is a reproduction of the multiplet between δ 2.6 and δ 2.8. Analyze this multiplet as the AB part of an ABX pattern, using the peak positions (in Hz) shown. Calculate accurate coupling constants and chemical shifts. If there is more than one solution, present both. Show your work, and tabulate your data in an easily readable form.

1	726.4	$c_- = (5+3)/2 = 746.7$	
2	738.2	$c_+ = (6+4)/2 = 755.45$	
3	742.5		
4	754.5	$\Delta\nu_{ab-} = \text{sqrt}((7-1)(5-3)) = 18.5$	$c_- \pm \nu/2 = 755.9, 737.5$
5	750.9	$\Delta\nu_{ab+} = \text{sqrt}((8-2)(6-4)) = 8.11$	$c_+ \pm \nu/2 = 759.5, 751.4$
6	756.4		
7	767.1		
8	772.8		

NMR Data

Solution 1

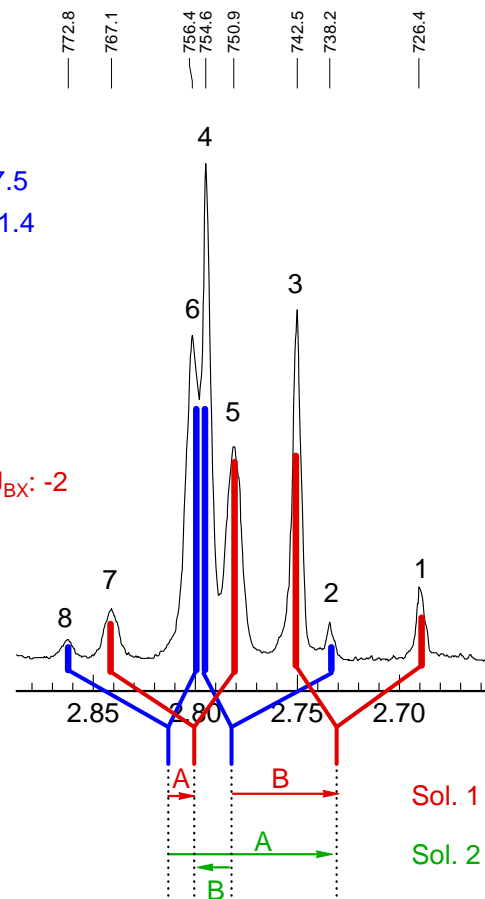
$J_{AB} = 16.1$
 $J_{AX} = 3.6$
 $J_{BX} = 13.9$
 $\nu_A = 757.7$
 $\nu_B = 744.4$
 $\Delta\nu_{AB} = 13.3$
 $\delta_A = 2.81$
 $\delta_B = 2.76$

Solution 2

$J_{AB} = 16.1$
 $J_{AX} = -22.0$
 $J_{BX} = +4.5$
 $\nu_A = 748.5$
 $\nu_B = 753.7$
 $\Delta\nu_{AB} = 5.2$
 $\delta_A = 2.77$
 $\delta_B = 2.79$

No or incorrect JAB: -2

Missing or wrong sign J_{AX}/J_{BX} : -2



Intensity Calculation

Solution 1

$\Phi_{1+} = 0.5 \arcsin(J_{AB}/2D+) = 31.8$
 $\Phi_{1-} = 0.5 \arcsin(J_{AB}/2D-) = 20.4$
 $i_{10} = i_{11} = 0.96$
 $i_{14} = i_{15} = 0.04$

Solution 2

$\Phi_{2+} = \Phi_{1+} = 31.8$
 $\Phi_{2-} = 90 - \Phi_{1-} = 69.6$
 $i_{10} = i_{11} = 0.62$
 $i_{14} = i_{15} = 0.38$

(f) Since the X-part is complicated by additional coupling (it's really an ABMNXY pattern), suggest ways to distinguish between solutions 1 and 2?

Sign of J_{AX} and J_{BX} couplings is OK for Sol. 1 (all positive), not so for Sol. 2 (3J are all positive). Magnitude of couplings is possible for both solutions, but better for Sol. 1. Intensity calculation gives 0.38/0.62 ratio. The X peak (H_5) is well behaved, and this also suggests Solution 1.

There is also the broadening of the peaks - the four signals for A are all broadened significantly compared to those for B in Sol 1 (they share a coupling partner). This is not the case for Sol 2.