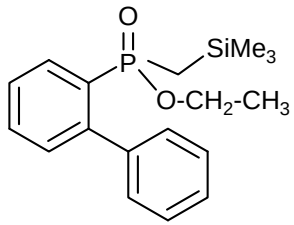
Problem R-13E ($C_{18}H_{25}O_2PSi$)

300.1 MHz ^1H NMR Spectrum in $CDCl_3$.

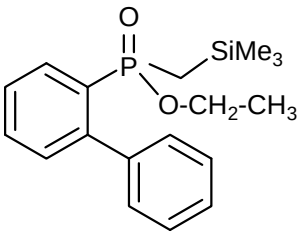
Source:Olafs Daugulis/Vedejs digitized hard copy 08/24 g



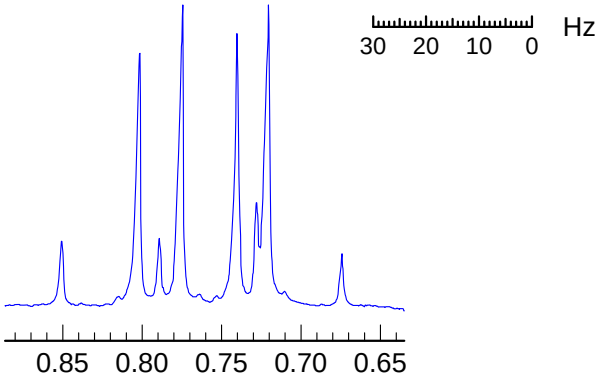
PLT ex-2-2013-14-g.plt

Problem R-13E ($C_{18}H_{25}O_2PSi$). In this problem you are given the structure of a phosphorus compound and asked to interpret parts of the NMR spectrum. For each multiplet or set of multiplets report the pattern in the standard format: δ 0.00, triplet of pentets, $^{n}J_{XY}$ = 0.0 Hz. You may use first order analysis.

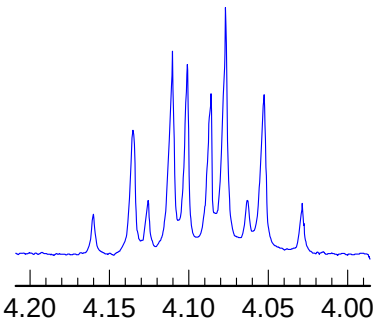
(a) Assign and interpret the three signals centered at δ -0.05.

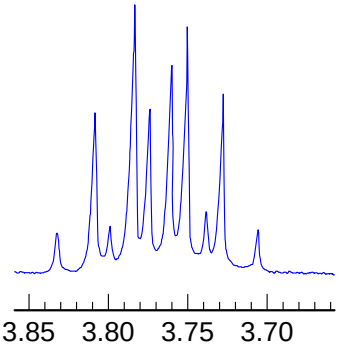


(b) Assign and interpret the multiplet at δ 0.75. Draw and label a coupling tree.

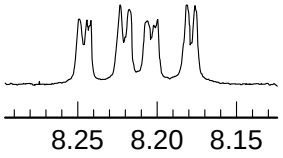


(c) Assign and interpret the multiplets at δ 3.7 - 4.2. Draw and label a coupling tree.





(d) Assign and interpret the multiplet at δ 8.2.



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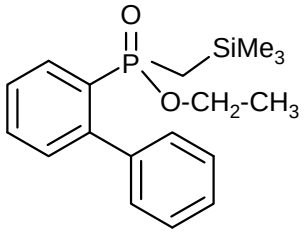


(a) Assign and interpret the three signals centered at δ -0.05.

Me_3Si signal

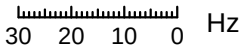
4 The two small peaks are ^{29}Si satellites. There is no dtetectable coupling to ^{31}P

$^{2}J_{H\text{-}Si}$ = 7Hz

(b) Assign and interpret the multiplet at δ 0.75. Draw and label a coupling tree.

This is the P-$\underline{CH_2}$-$SiMe_3$ group - the protons are diastereotopic (P is an asymmetric center), so this is an $\underline{AB}$X pattern X = ^{31}P

J_{AB} = 14 Hz ($^{2}J_{HH}$)



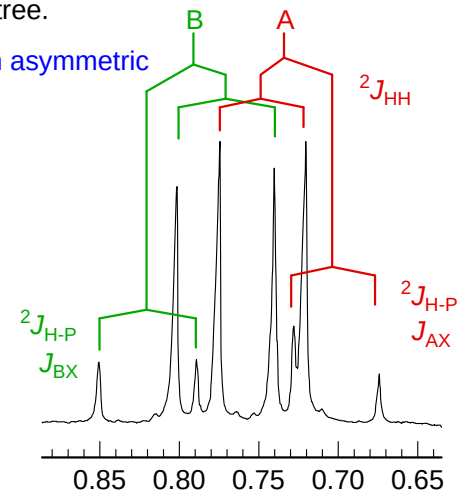
δ_A = 0.73

J_{AX} = 16 Hz ($^{2}J_{H\text{-}P}$)

7 δ_B = 0.78

J_{BX} = 18 Hz ($^{2}J_{H\text{-}P}$)

(this is "AMX" treatment which always corresponds to Solution1, not a proper ABX analysis, so if this happens to be a Solution 2 situation, then the J's would be very wrong - they do look OK though, and so Solution 1 is probably fine)



(c) Assign and interpret the multiplets at δ 3.7 - 4.2. Draw and label a coupling tree.

$\underline{AB}M_3X$

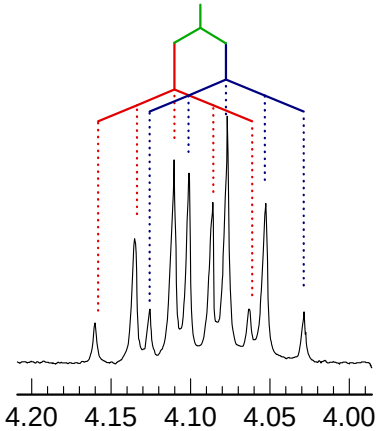
Each pattern is a doublet of pentets, J = 10, 7 Hz for the diastereotopic O-$\underline{CH_2}$-CH_3 group. The pentet arises because $^{3}J_{HH}$ to the CH_3 group and $^{3}J_{HP}$ are nearly the same

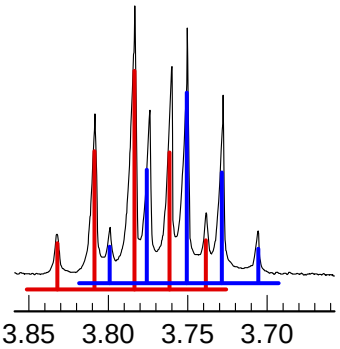
6 $^{3}J_{HH}$ = 7 Hz

$^{3}J_{HP}$ = 7 Hz

$^{2}J_{HH}$ = 10 Hz

We know the 10 Hz coupling is the gem J_{HH} because of the size, and leaning effects.





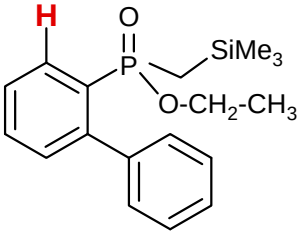
(d) Assign and interpret the multiplet at δ 8.2.

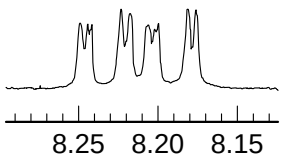
This must be the proton ortho to the phosphonate group - approximately a ddd, J = 12, 6, 2 Hz. There are some second-order effects, so couplings are suspect

3 $^{3}J_{HH}$ = 8 Hz (ortho coupling)

$^{4}J_{HH}$ = 2 Hz (meta coupling)

$^{3}J_{HP}$ = 12 Hz (ortho ^{31}P coupling)





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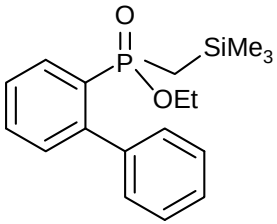
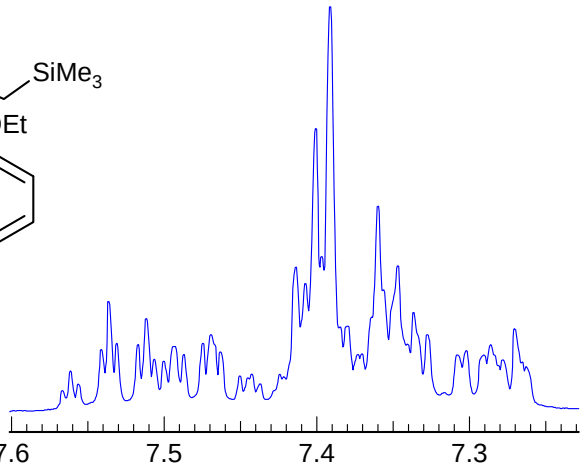
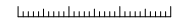
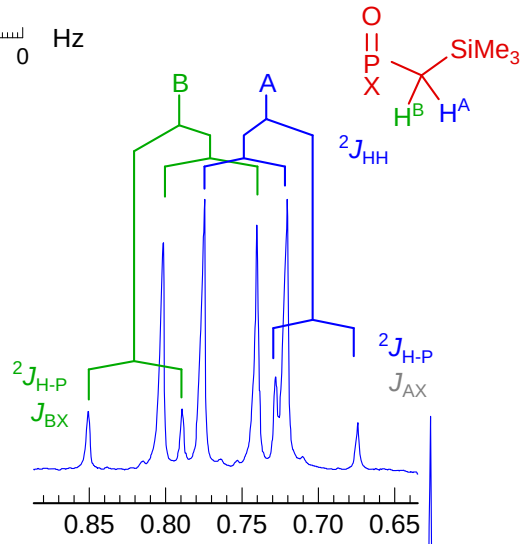
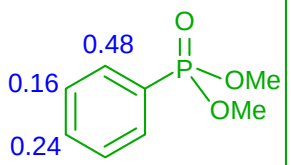


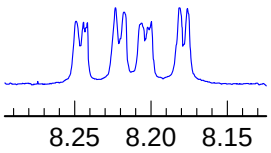






Benzene Shifts





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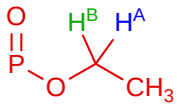
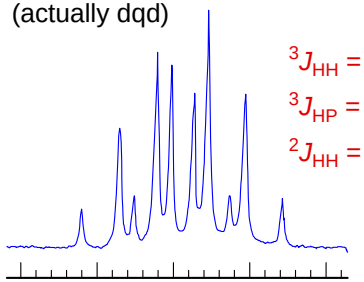
d pentets
(actually dqd)





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$^3J_{HP}$ = 7 Hz

$^2J_{HH}$ = 10 Hz

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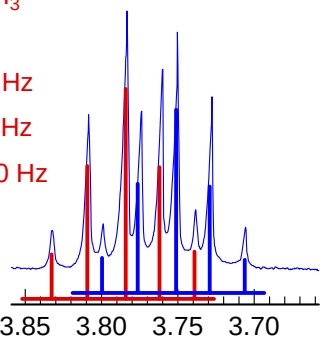

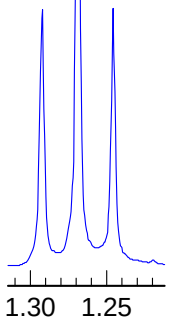

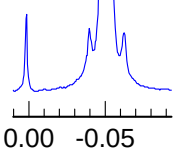

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