NMR STUDY OF n-PROPYLLITHIUM AGGREGATES

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A variable temperature ^{1}H, ^{13}C, and ^{6}Li NMR study of n-propyl-^{6}Li-lithium showed five different aggregates, similar to that in the literature as $(RLi)_n$, n= 6, 8, 9, 9, 9. There were also a number of additional new species, identified as lithium hydride containing aggregates. Unexpectedly, a series of $^{13}C\{^{1}H\}$ 1-D NMR experiments with selective ^{6}Li decoupling showed evidence for ^{13}C-^{6}Li spin-spin coupling between the previously reported $(RLi)_n$ aggregates and various hydride species.

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CHAPTER I

INTRODUCTION

Organolithium reagents are used in many organic and polymeric syntheses.[1-6] For instance, they alkylate compounds with differing organic functional groups. Organolithiums act as very strong bases. This finds use in anionic polymerization.[7-9] The synthetic uses are available commercially for pharmaceutical manufacturing as well.[10]

Despite their widespread use, many structures are still unresolved. There are numerous studies regarding alkyllithiums using solid-state,[11-14] theoretical calculations,[15-19] and Nuclear Magnetic Resonance(NMR) studies.[20-30] Although there is much information for organolithiums, the solution structures are not completely understood. There are differences in structure and dynamics between the solid and liquid state. More of the syntheses for organolithiums occur in solution than in solid state. Studying organolithiums in the solution phase is necessary. Therefore, NMR can be used to study these compounds.

Alkyllithiums in solution have the general formula, $(RLi)_n$, where n is the aggregation state. The aggregation state, n, has been observed to exist anywhere from one to nine,[20,23,31] depending upon the temperature, solvent, concentration, and the specific R group attached. Additionally, more than one aggregate can exist in solution.

The temperature dependence affects the aggregation formation. For a non-coordinating solvent, the aggregation increases as the temperature decreases. The opposite is seen with a coordinating solvent, where aggregation decreases as temperature decreases. The concentration also affects the aggregation of the alkyllithium. As the concentration increases so does the aggregation.

Using different types of alkyl groups affects the degree of aggregation. If the alkyl group is small, with no steric hindrance, the alkyllithium favors higher aggregates in solution. However, larger alkyl groups with more steric hindrance favor lower aggregates. In a hydrocarbon solvent, t-butyllithium exists only as a tetramer[32]. In a hydrocarbon solvent, n-propyllithium exists as a hexamer at 273K[23].

NMR spectroscopy reveals much about alkyllithium compounds.[20- 26] For instance, one can focus attention on the alpha (c1, α) carbon and lithium nuclei. The ^{13}C and ^{6}Li NMR spectra reveal the different aggregates in solution. A ^{13}C NMR spectrum with a fluxional aggregate shows the multiplicity and coupling constants. This information can reveal the aggregation of the compound. Based on experimental ^{13}C-^{6}Li coupling constants, a formula was derived to determine the aggregation states of alkyllithium compounds

$$J_{(^{13}C-^{6}Li)} = (17 \pm 2)\ \mathrm{Hz}/n$$

where n is the number of equivalently bonded ^{6}Li nuclei.[33-34] This does not give a definite answer on the aggregation. Results have shown this formula works well for small and less bulky alkyl groups like the n-propyllithium system. In sterically hindered groups this method is not as reliable.[20]

The compound studied in this work is n-propyllithium. This is a straight chain organolithium similar to n-butyllithium. The n-butyllithium system is very common in catalytic processes. However, the aggregation states are difficult to examine in ^{13}C NMR spectra. There is no coupling present in the c1 region of n-butyllithium so the aggregates are difficult to examine. The n-propyllithium system is helpful because of its coupling data. The aggregation states of n-propyllithium should be similar to n-butyllithium.

The n-propyllithium compound has one aggregate at room temperature. This is reported as a hexamer. Fraenkel reported five different aggregates below 230K.[23] These include a hexamer, an octamer and three different nonamers. There was a range of distributions for the aggregates depending upon the temperature. Equilibrium and thermodynamic data supported the aggregation states distribution. Fraenkel's aggregation states were obtained directly from coupling constants.[13] Additionally, this system was enriched with ^{13}C, on the alpha carbon, and ^{6}Li to improve line shape analysis. This report was interesting because it gives four aggregates larger than six. The information was based on coupling constants.

Don Ellington confirms the three major aggregates.[35] Little is known about the minor nonamer aggregates. The purpose of this work is to resolve the minor nonamer aggregates. This will complement the work for the n-propyllithium system, ultimately leading to a better understanding of the aggregation states for the n-butyllithium system.

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CHAPTER II

EXPERIMENTS

Introduction

The organomercury compound, $(CH_3CH_2CH_2)_2Hg$ in step 2, was prepared by previous group members. The general synthesis of this compound follows:

$$RX + Mg \rightarrow RMgX \qquad [1]$$

$$2\,RMgX + HgX_2 \rightarrow HgR_2 + 2\,MgX_2 \qquad [2]$$

$$HgR_2 + 2\,{}^6Li \rightarrow 2\,R^6Li + Hg \qquad [3]$$

where, X= Halide and R= $CH_3CH_2CH_2$-.

Steps [1] and [2] are found elsewhere[1-3]. This synthetic route prevents halide contamination in step [3]. This allows no halide interaction with the alkyllithium. The lithium metal was enriched to 95.5% ^6Li[4].

Precaution when using $(n\text{-}Pr)_2Hg$

Organomercury compounds can affect the nervous system[5]; therefore, all work was conducted under a hood, on a protected vacuum line or in the dry box. All glassware used with organomercury compounds was washed in concentrated nitric acid, cleaned and dried in an oven at 523K.

Distillation of $(n\text{-}Pr)_2Hg$

The $(n\text{-}Pr)_2Hg$ was kept refrigerated and covered with foil to prevent decomposition. Previous samples prepared by Hanh Nguyen and He Huang were combined for this distillation. The total volume used in this step was 25.59mL. This was weighed out under a hood. Then the $(n\text{-}Pr)_2Hg$ was added to a 100mL pot that was then connected to a vacuum distillation apparatus.

At the final evacuation, the distillation was performed at 75°C and 10 torr. The initial 24 drops of $(n\text{-}Pr)_2Hg$ were discarded. This was considered to contain impurities. An additional receiver flask was used for the next fraction of $(n\text{-}Pr)_2Hg$. A sample was prepared with $CDCl_3$ to a concentration of 1M.

A ^{13}C Nuclear Magnetic Resonance(NMR) spectrum was run for each sample using the Varian VXR® 300MHz NMR instrument. The spectrum shows only peaks referring to $CDCl_3$ and $(n\text{-}Pr)_2Hg$. The $CDCl_3$ resonance is referenced at 77.00ppm. The $(n\text{-}Pr)_2Hg$ system has three resonances. The ^{13}C chemical shifts with coupling constants for the $(n\text{-}Pr)_2Hg$ compound prepared and two references, one by Jensen[7] and the other by Terence N. Mitchell and Heinrich C. Marsmann,[8] are in Table 1. Both samples from the two flasks were considered clean for transmetallation (step 3).

Table 1: ^{13}C Chemical Shifts (ppm) of $(n\text{-}Pr)_2Hg$

^{13}C Chemical Shifts (ppm) of $(n\text{-}Pr)_2Hg$ (Coupling Constants, Hz)			
c-1	c-2	c-3	Reference
47.25(661)	22.33(25.7)	19.87(103)	Present work, a
47.3(665)	22.7(24)	20.1(104)	Jensen,[7] b
47.25(658)	22.33(26)	19.80(103)	Mitchell and Heinrich,[8] c

(a) Referenced to TMS by setting $CDCl_3$ 77.00ppm
(b) Referenced to TMS by setting C_6D_6 to 128.00ppm
(c) In C_6D_6 with internal reference TMS at 0ppm

Description of a Freeze-Pump-Thaw Cycle

Initially the entire vacuum line was checked for any leaks. A tesla coil was used to find these leaks. An intense bluish-white spark is evidence of leaks or pinholes in the glassware. No leaks in the glassware were detected during the check.

The water gauge next to the manometer was turned on. A hose was connected from the vacuum line to the faucet. This is used in order to bring the mercury down from the manometer. The vacuum line has a continuous pump with a constant pressure of 1×10^{-3} torr. After the joints were checked, the two U-traps were covered with a dewar filled 2/3 full with isopropyl alcohol. This solution was cooled with dry ice chips. The chips were smashed to a fine powder so that the solution would stay constant throughout the dewar. Approximately four pounds of dry ice is suitable for both U-traps.

Once the U-traps were cooled carefully, the diffusion pump was turned on to reduce the pressure in the vacuum line even more. The switch on the power supply was set at 120V and 50% capacity. This was allowed to stand for a minimum of half an hour. The pressure read $5x10^{-6}$ torr with all joints closed. After the line reached this reading, one joint was open at a time and equilibrated until the pressure held $5x10^{-6}$ torr. This continued until all joints leading to the vessel stopcocks were open.

Next the overhead lights were turned off and the blinds were closed to prevent exposure to light for the organomercury compounds. This prevents any unwanted byproducts from forming. Light can cause the mercury carbon bond to break allowing for alkanes and alkenes to form. Following that the foil was uncovered from the vessels and placed on the vacuum line with the stopcocks closed. Rubber bands held the vessels in place to prevent any sudden pressure change with the line. Small dewars were filled with liquid N_2 and used to prevent any loss of the solution during the pump cycles.

Once the freezing was complete, the vessel was evacuated by opening the stopcock and allowing it to equilibrate for at least half an hour at $5x10^{-6}$ torr. After that the reaction vessel stopcock was closed and the dewar taken off the vessel. The vessel thawed for about half an hour. This F-P-T cycle was repeated as necessary.

Transmetallation of $(n\text{-}Pr)_2Hg$ to $n\text{-}Pr^6Li$

This process was performed inside an argon filled dry box to minimize $O_{2(g)}$ exposure. Transmetallation took place inside a reaction vessel. The reaction vessel was about 250mL, cylindrical and rounded. The vessel had a male joint attached to it. The neck was about six inches to allow for a flame seal.

Approximately 1.0g ^6Li_s (0.167 mol), 22.5g of dry cyclopentane (0.32 mol), 27.3g of $(n\text{-}Pr)_2Hg$ (0.042 mol) and broken glass chips were added to a reaction vessel. The 22.5g of cyclopentane was dried before use by lithium aluminum hydride in a storage vessel and allowed to mix in an argon atmosphere, covered with foil for 24 hours. This was then evacuated on the vacuum line and distilled to another storage vessel. Later placed in the dry box for transmetallation.

The ^6Li_s metal was carefully cut into small chips approximately 1 mm^3 in volume. This allows more surface area exposure during transmetallation. Approximately 1.0g, a 4 molar excess, of ^6Li_s was used to allow for a complete removal of the alkyl group from Hg.

Next, a mass of 22.5g from dried cyclopentane was added to the reaction vessel. Then, the $(n\text{-}Pr)_2Hg$ was added. Followed by the last 10 mL of cyclopentane to wash the pipette of any residual $(n\text{-}Pr)_2Hg$. Precautions were taken to not poison the catalyst in the box by adding the $(n\text{-}Pr)_2Hg$ last by minimizing exposure to the dry box atmosphere.

This reaction vessel was then quickly capped with a male/female glass joint and taken to a high vacuum line. There, the heterogeneous solution was freeze-pump-thawed nine times to a pressure of $5x10^{-6}$ torr.

On the tenth pump the reaction vessel was flame sealed. This was then covered with foil and allowed to warm up to room temperature overnight in a hood. The next day the reaction vessel was checked visually for air leaks. Then the vessel was placed on a shaker for four weeks.

After the fourth week the vessel was taken back into the dry box. Inside the box, the vessel was carefully broken at the neck. A sample was extracted from the reaction vessel and placed in an NMR tube with a rubber septum to prevent exposure to oxygen. Then the solution was checked for unwanted $(n\text{-}Pr)_2Hg$ by running a ^{13}C NMR experiment. The ^{13}C NMR spectrum showed the chemical shift for $(n\text{-}Pr)_2Hg$. This solution mixture was put into a new reaction vessel with new $^{6}Li_{s}$ metal. An additional 10 mL of dry cyclopentane was used to clean out the old reaction vessel. The entire F-P-T process was performed again then flame sealed and set on the shaker for two more weeks. At the end of the two weeks the ^{13}C NMR spectrum showed no evidence for $(n\text{-}Pr)_2Hg$.

Removal of Cyclopentane from n-$Pr^{6}Li$

All of the following procedures were performed in the dry box and on the high vacuum line. Once the solution was checked by ^{13}C NMR for unwanted $(n\text{-}Pr)_2Hg$, a filtration was performed using a coarse glass frit. This solution, n-$Pr^{6}Li$, was placed inside a clean storage vessel, approximately 50mL, and placed on the high vacuum line to pull off the cyclopentane.

Two vessels were placed on the vacuum line for a vacuum distillation. One contained nothing in it. This was used for the cyclopentane transfer. The second vessel contained the solution of n-$Pr^{6}Li$. Initially, both vessels were pumped down to $5x10^{-6}$torr. Next, the vacuum line was closed and the cyclopentane was slowly transferred to the empty vessel. The cyclopentane was taken off the line and disposed into a hazardous waste container. Next the vacuum line was opened and the pressure was lowered to $5x10^{-6}$ torr. The storage vessel with just the n-$Pr^{6}Li$ was then F-P-T three times to $5x10^{-6}$ torr and then flame sealed for later use.

Preparation of [n-$Pr^{6}Li$]=2M Solution

Inside the dry box, a solution of n-$Pr^{6}Li$ was made in the following manner. The storage vessel containing the n-$Pr^{6}Li$ was broken open. Approximately 0.069g of n-$Pr^{6}Li$ was weighed out into a 25mL Erlenmeyer flask. Next, a mass of 0.531g of dry 10%

deuterated cyclopentane solution was added to the same flask. This was quickly swirled and put into a 5mm NMR tube with a male joint. This was then capped with a stopcock and placed onto the high vacuum line. There the NMR tube was F-P-T four times. Next the NMR tube was flame sealed. Each pump measured down to $5x10^{-6}$ torr.

The additional n-Pr^6Li solution was placed inside a new storage vessel. The storage vessel was placed on the vacuum line. This solution was F-P-T four times and finally flame sealed for later use. Additional precautions and procedures on how to handle the alkyllithium have been discussed in other theses.[3, 6, 9, 10] They include procedures on how to handle glassware, using the antichamber and regeneration of the dry box.

Preparation of the NMR Solvent and Other Reagents

The 10%-deuterated cyclopentane served as the solvent for NMR study. The deuterated solvent provides for a lock signal. However this compound is very expensive and a minimum amount was diluted with dry cyclopentane. Additional procedures on how the solvent was made are as follows. Two solutions, cyclopentane (90 mL) and deuterated cyclopentane (10 mL), were place in storage vessels with approximately 2g of $LiAlH_4$ as a drying agent. These solutions were evacuated and sat overnight. The solutions were placed on the vacuum line and transferred to new storage vessels. Then these vessels were taken into the dry-box where they were diluted to 10%-deuterated cyclopentane. This was the stock for all NMR solutions.

Description of the NMR Experiments

All data were acquired on a Varian VXR® 300 NMR spectrometer. Additional work was achieved on a modified triple resonance probe (TRP). This 10mm probe has a

^{6}Li decoupling coil substituted for the lock coil. A more detailed description of the hardware is described elsewhere[10].

^{1}H, ^{13}C, ^{6}Li 1-D NMR Spectral Parameters

Most of the 1-D NMR spectra were obtained with the 5mm tunable probe. The parameters for the ^{1}H (300MHz) NMR spectra are as follows. The sweep width used was 4000.0 Hz. The acquisition time was set to 3.752 seconds. The pulse width was set at 1°. The transmitter offset was at 700Hz. There was no delay. Only 16 transients were collected. The chemical shifts were assigned by referencing the cyclopentane resonance at 1.51ppm.

The ^{13}C (75 MHz) NMR parameters are as follows. The sweep width was set to 17000 Hertz. The pulse width was set at 30°. The acquisition time was 0.882 seconds. The offset was set to 1000 Hertz. There was no delay. Each experiment accumulated 1280 transients. The spectra were referenced to the protonated cyclopentane resonance at 25.89ppm.

The ^{6}Li (44 MHz) coupled and decoupled NMR parameters were as follows. The spectral width was set at 500 Hz. The acquisition time was set for 9.9 seconds with a delay of 30 seconds between each transient. The pulse width was set at 90°. Each spectrum was acquired for 32 transients. The spectra were referenced to n-propyllithium's main resonance at room temperature, which is 0ppm. This is the hexamer aggregate.

For the ^{6}Li decoupled experiments, the decoupler was switched on during the acquisition and off during the 30 second delay. The command on the software DM=NNY was used to properly integrate and decouple the resonances in the spectra. The command with DM=YYY was used to increase the intensities of all the resonances in the sample. Coupled experiments were performed as well. The command for the coupled experiments was DM=NNN. To enhance the smaller signals in coupled experiments, the command DM=YYN was used.

2-D ^{6}Li- ^{1}H Heteronuclear Overhauser Effect Spectroscopy (HOESY)

One of the 2-D NMR experiments included the Heteronuclear Overhauser Effect Spectroscopy (HOESY). This experiment ran on the 5mm tunable probe. The parameters for this experiment included spectral windows of 120Hz and 500Hz for the ^{6}Li and ^{1}H, respectively. The ^{6}Li 90° and 180° pulses used and measured were 21.5 and 43.0 μseconds. The acquisition was 1.33 seconds, with 32 transients. The delay was set to 3 seconds, with a mixing time of 1 second. The ^{1}H polarization transfer pulse was set to 19.4 μseconds, with 128 increments.

2-D ^{13}C-^{6}Li Heteronuclear Correlation Spectroscopy (HETCOR)

Another valuable NMR experiment performed was the ^{13}C-^{6}Li Heteronuclear Correlation (HETCOR). This is a modified experiment on the 10mm TRP. This experiment ran at 214K. A description on how this was accomplished follows. The first step was to lower the temperature to 214K. A methanol sample determined the corrected temperature. The methanol was taken out and the n-Pr^{6}Li sample equilibrated to 214K for approximately one hour. Next, the shimming of the sample was adjusted to create a homogeneous magnetic field within the sample. The ^{1}H spectrum was used in conjunction with shimming. The cyclopentane peak line width at half height was 0.4 Hz. Next, a ^{6}Li experiment was run through the ^{6}Li decoupler. The spectral window and transmitter offset moved to allow for a better spectrum. This spectrum determines the desired frequency for any ^{6}Li peak. A series of frequencies were calculated. The main nonamer at –0.166ppm in the ^{6}Li{^{1}H} NMR spectrum was determined first. This value was determined by the command SETDMX. This command calculated a value of 804. The value was manually set on the ^{6}Li decoupler. The attenuator was set to 0 so that all ^{6}Li nuclei decouple. A ^{13}C{^{6}Li, ^{1}H} experiment showed all n-propyllithium c1 resonances collapsed to single sharp peaks. The ^{13}C{^{6}Li, ^{1}H} spectral width shortened and transmitter offset moved to cover 0ppm to 40ppm. The parameters for the ^{13}C-^{6}Li HETCOR were transferred to EXP8 under the MACRO file C13LI6. The parameters for the ^{13}C and ^{6}Li 1-D experiments were transferred by the command GETHCR. Once the parameters were set, the experiment began.

The ^{13}C parameters were as follows. The sweep width was reduced to 2092Hz (F2). This ranged from 0ppm to 28ppm. There was a 90° pulse with an acquisition time of 2.3 seconds and a D1 delay of 10 seconds. There were 64 transients accumulated with NI=128. Some ^{6}Li parameters were modified as well. The F1 dimension was 200 Hz that included all resonances with a 90° pulse.

1-D ^{13}C{^{6}Li, ^{1}H} NMR Selective Decoupling at 214K

A series of ^{13}C{^{6}Li, ^{1}H} NMR experiments were collected with the attenuator at different levels. The series ran at 214K. The series began with the attenuator at 01, 02, …, and 10. The purpose was to decouple only the region specified. Setting the attenuator at 04 gave the best result. Only the c1 nonamer peak collapsed, the others are broad. Levels 01, 02, 03 showed all c1 peaks collapse, 05 and beyond show no peaks collapse. The decoupler was set to different peaks in the ^{6}Li spectrum with the attenuator set to 04.

Low Temperature Experiments

These experiments were performed with the methanol sample command (TEMCAL(M)). A ^{1}H experiment was used to calibrate the temperature.[11] The temperature was determined from the difference in chemical shift between the methyl ^{1}H's and the hydroxyl ^{1}H. This difference increases as the temperature lowered. The temperature parameter changed from TEMP=N to TEMP=15ºC in the experiment. A nitrogen gas line must be used for low temperature experiments. This was allowed to run with TEMP=15ºC for approximately 30 minutes. This allowed for the removal of oxygen and water in the NMR line. Next, a dewar was placed on the coil where the nitrogen gas line passed through into the NMR. The dewar was filled with liquid nitrogen. After the temperature settled for roughly 10 minutes at TEMP=15ºC, the temperature was lowered by 10ºC to TEMP=5ºC. This was systematically done down to the desired temperature of 214K. One thing to note was that the NMR temperature was different from the TEMP reading. This also varied with each probe. Table 2 lists the nuclei and their relative temperatures in the 5mm probe.

Table 2: Temperature Differences

Panel reading	^{1}H(K), ^{6}Li(coupled and decoupled, K)	^{13}C(decoupled, K)
291	291	295
273	259	263
268	252	257
263	246	251
258	238	243
253	232	237
248	226	231
243	220	225
238	214	218
233	207	210
228	199	205
223	194	198

These were the temperatures obtained during the variable temperature series of n-PrLi.

The temperature was set to 214K on 10mm TRP for this work.

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CHAPTER III

RESULTS AND DISCUSSION

The compound under investigation was n-propyllithium. The following is a representation

$$\mathrm{Li}-\underset{\mathrm{c1}}{\overset{\alpha}{\mathrm{CH_2}}}-\underset{\mathrm{c2}}{\overset{\beta}{\mathrm{CH_2}}}-\underset{\mathrm{c3}}{\overset{\gamma}{\mathrm{CH_3}}}$$

The initial step was to acquire ^{1}H, ^{13}C and ^{6}Li Nuclear Magentic Resonance(NMR) spectra at various temperatures and compare to Fraenkel's data.[1] These experiments were carried out using 5mm NMR tubes on the 5mm tunable probe.

^{1}H 1-D NMR Spectrum at 291K

The ^{1}H NMR spectrum at 291K has four resonances (Figure 1). A singlet resonance at 1.51ppm corresponds to the protons from the cyclopentane solvents. It has a very strong resonance due to the 9:1 ratio of protonated to deuterated cyclopentane in solution. Next to this resonance is a multiplet at 1.41ppm. This corresponds to the protons on carbon c2. Upfield from this is a triplet centered at 1.07ppm. This corresponds to the protons on carbon c3. The fourth resonance centered at -0.81ppm corresponds to the protons on carbon c1.

The ^{1}H NMR spectrum has only one major alkyl aggregate present at this temperature. If there were other aggregates, then additional multiplets would appear in the spectrum at the c1, c2, and c3 proton regions.

^{13}C 1-D NMR Spectrum at 291K

The ^{13}C NMR spectrum at 291K (Figure 2) shows five resonances. There is a strong solvent resonance present at 25.89ppm relative to TMS. At 25ppm, a multiplet corresponds to the deuterated cyclopentane. Immediately upfield are carbons c2 and c3 resonances at 23.3ppm and 23.2ppm, respectively. Thomas reports c2 and c3 resonances at 22.4ppm and 22.3ppm, respectively.[2] The reference for Thomas[2] was the deuterated cyclopentane at 25.8ppm. But the main point is that the c2 is further upfield versus the c3 carbon.

Further upfield is the resonance at 16.21ppm. This corresponds to carbon c1. It is a broad single resonance. This is due to unresolved coupling between the ^{13}C and ^{6}Li nuclei in the aggregate. This is the hexamer aggregate reported by Fraenkel[1] and Thomas.[2] Jensen reported the c1 resonance at 16.1ppm at 293K in cyclopentane at 22.53MHz.[3] There are two small resonances that are near 18.00ppm and 18.11ppm. Delong[4] and Huang[5] report that n-propoxide has three resonances near 67ppm. The C=C moiety resonates near 130ppm. There is nothing near these resonances in Figure 2.

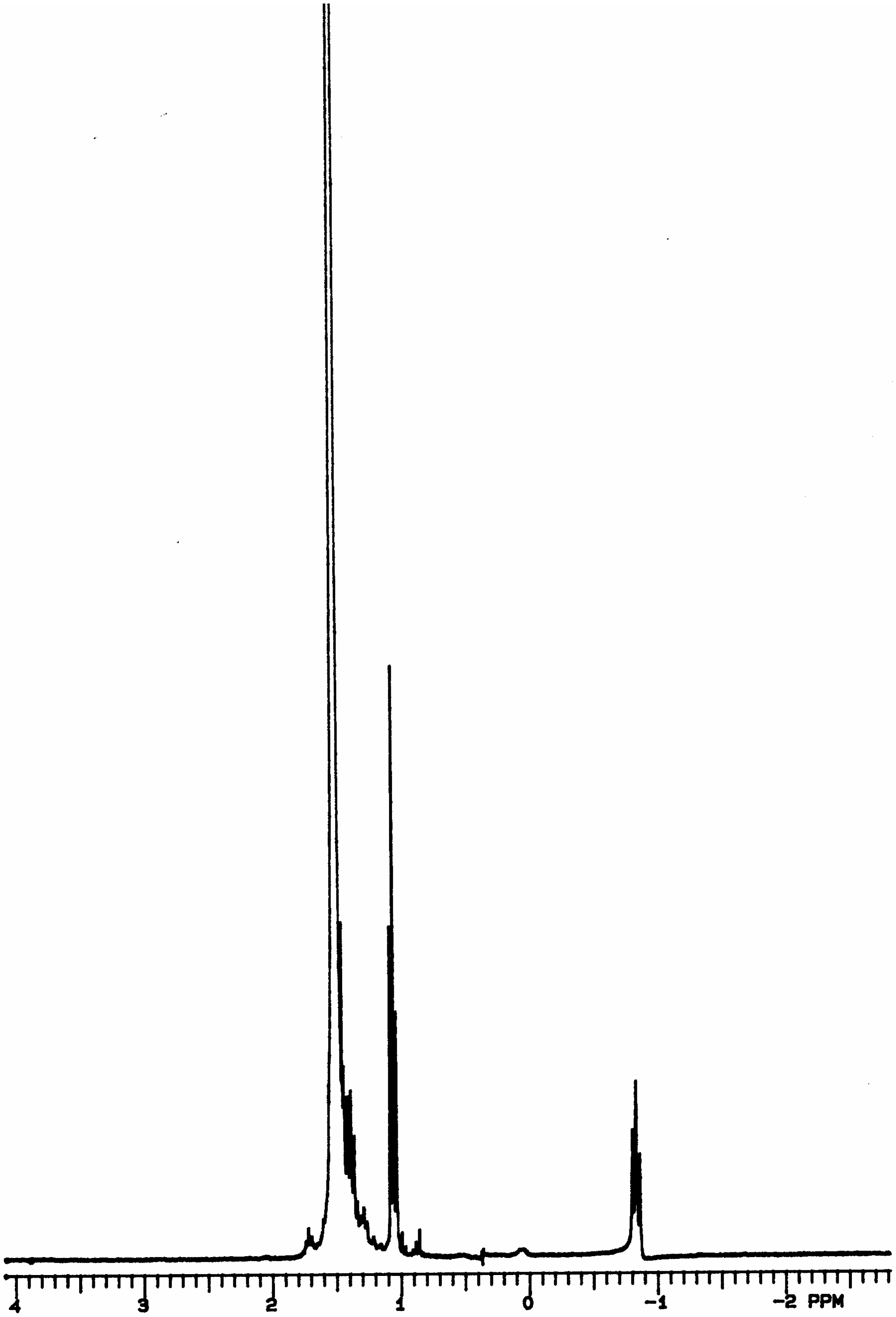

Figure 1– ^{1}H NMR Spectrum of n-propyllithium at 291K. The c1 ^{1}H region is at -0.81ppm; c3 at 1.07ppm; c2 at 1.41ppm; cyclopentane at 1.51ppm.

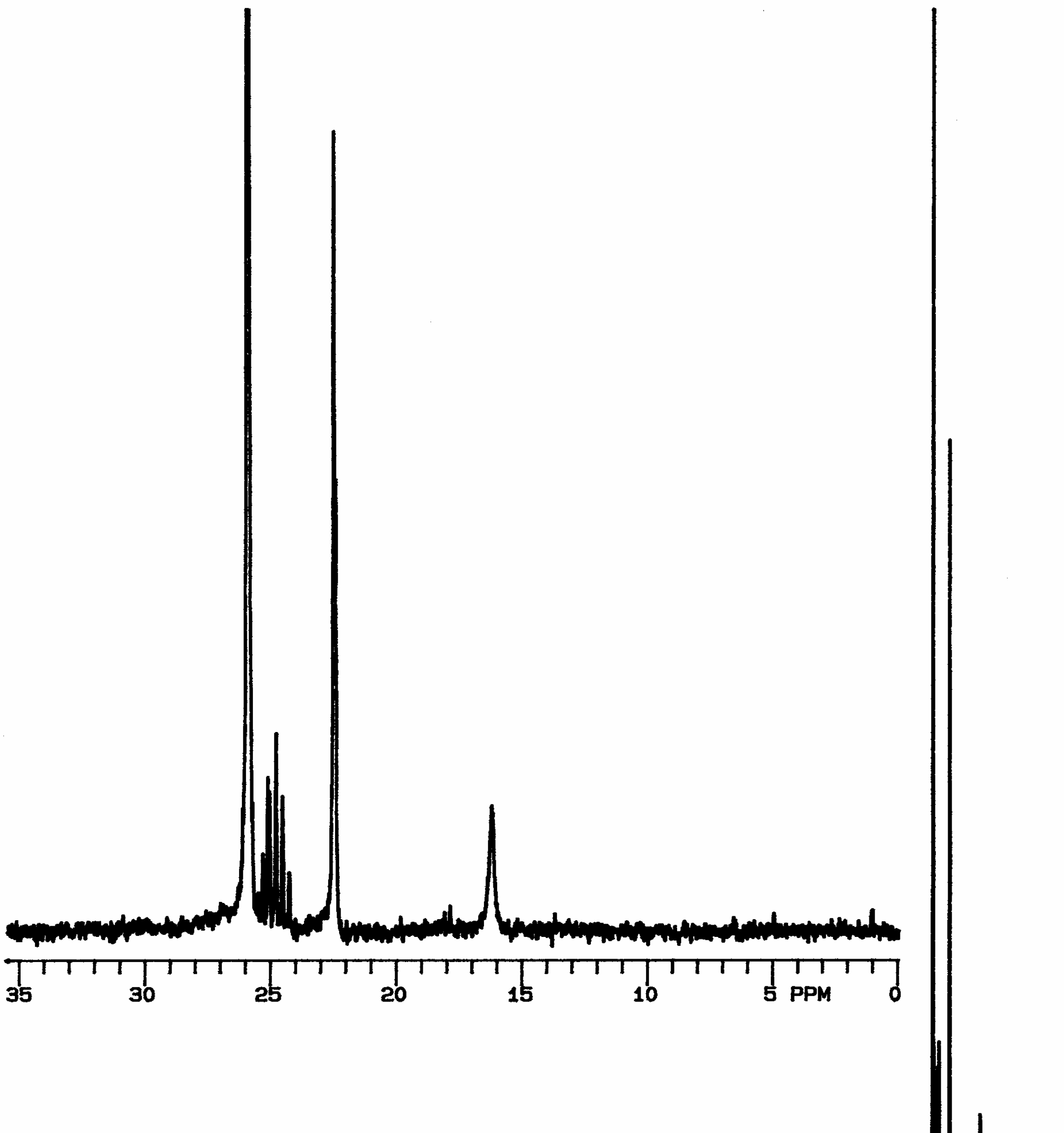

Figure 2– ^{13}C NMR Spectrum of n-propyllithium at 291K. Inset shows expanded c1, 16.21ppm, region.

^{6}Li 1-D NMR Spectrum at 291K

The ^{6}Li NMR spectrum at 291K (Figure 3) shows one major aggregate referenced at 0ppm (VS=500) and minor resonances in expansion at –0.60ppm and –0.92ppm (VS=5000). This further suggests one major magnetic environment is present at this temperature; the hexamer aggregate reported by Fraenkel.[1] The minor resonances are not far enough upfield to be considered lithium n-propoxide aggregates. He Huang reports that n-propoxide resonances occur at -2.0ppm referenced to the n-propyllithium resonance at 0ppm at room temperature.

^{1}H 1-D NMR Spectrum at 214K (Figure 4)

The ^{1}H NMR spectrum has four main regions, but these regions have changed in multiplicity versus the room temperature spectra. Starting upfield, there is an area of overlapping multiplets from -0.9 to -0.75ppm. This is the ^{1}H region for the c1 carbon for the different aggregates. Moving downfield to the next major region, there is another complex multiplet centered at 1.06ppm for the ^{1}H c3 carbon for the different aggregates. Further down field at 1.35ppm are the multiplets corresponding to the ^{1}H region for the c2 carbon for the different aggregates. The very large resonance at 1.51ppm is associated with cyclopentane ^{1}H's. The smaller resonances at 0.10ppm, 0.85ppm, 0.90ppm and 1.85ppm cannot be assigned with certainty.

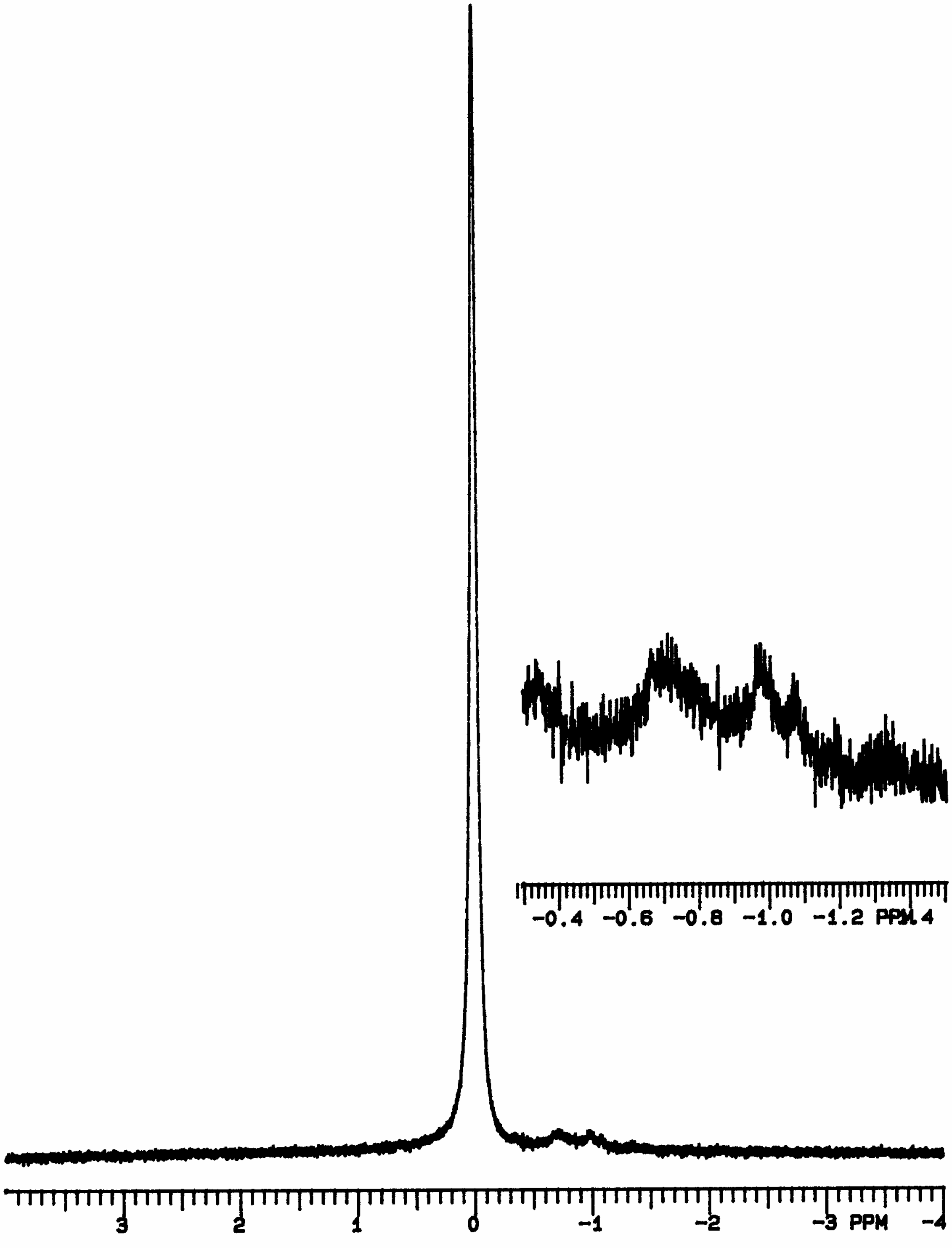

Figure 3– ^{6}Li NMR Spectrum of n-propyllithium at 291K. Inset shows expanded lithium hydride region.

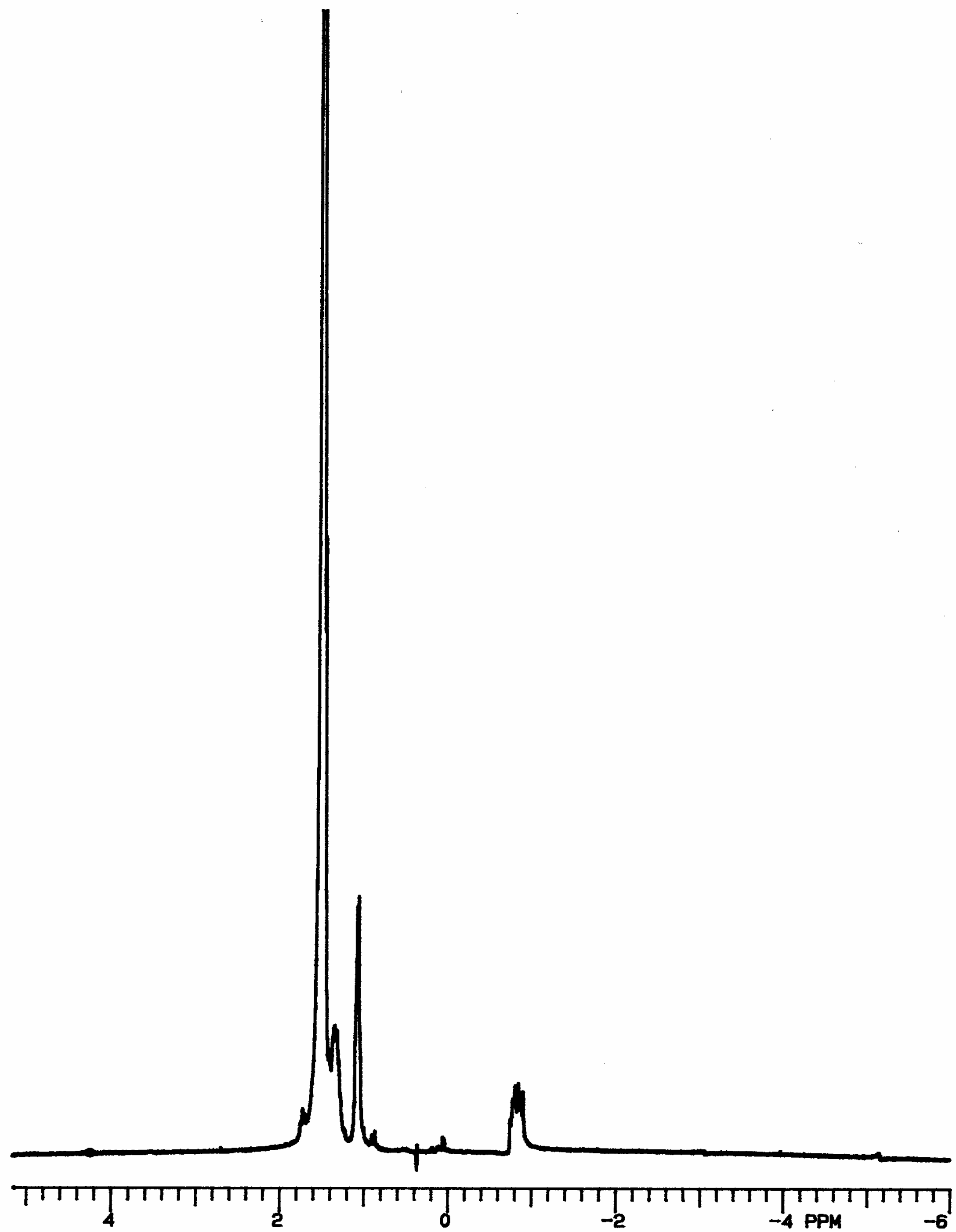

Figure 4– ^{1}H NMR Spectrum of n-propyllithium at 214K.

^{13}C 1-D NMR Spectrum at 214K (Figure 5)

The following table shows this work's results with Fraenkel[1], and Ellington[6] for the n-propyllithium system at 214K.

Table 3: ^{13}C Chemical Shift, ^{13}C-^{6}Li Coupling Constants and Aggregations of n-Propyllithium

Figure 5		Fraenkel[1]		Ellington[6]		Huang[5]		
δ	J (Hz)	δ	J(Hz)	δ	J(Hz)	δ	J(Hz)	Agg.
15.80	3.1	15.74	3.35	15.6	3.4	15.77	3.1	6
17.60	2.6	17.50	2.48	17.4	2.5	17.48	N/a	8
18.00	N/a	N/a	N/a	N/a	N/a	N/a	N/a	N/a
18.11	N/a	N/a	N/a	N/a	N/a	N/a	N/a	N/a
18.65	2.2	18.50	2.22	18.4	2.2	18.57	N/a	9
18.90	N/a	18.79	2.22	N/a	N/a	N/a	N/a	9
N/a	N/a	19.09	2.22	N/a	N/a	N/a	N/a	9

Following Fig.5 is Fraenkel's[1] data. Note his results were initially recorded only in Hertz. This table shows these calculated in and referenced by the hexamer aggregate according to this work. This column shows these results if Fraenkel's[1] hexamer aggregate was set to 15.80ppm as in Figure 5. The following column shows the coupling constants for the resonances. Fraenkel's[1] values were recorded with a [n-Pr^{6}Li]=0.5M at 217K. The spectra were run at 67.89 MHz for the ^{13}C NMR spectrum. These parameters were adjusted accordingly when converted to compare with this work's results.

The next two columns show Ellington's[6] ^{13}C NMR data for n-propyllithium at 183K. Then following are Huang's[5] results at 193K and a [n-Pr^{6}Li]=2.0M. The last column shows the aggregates for these resonances. Notice that there is only one nonamer aggregate for Ellington[6] and Huang[5] versus Fraenkel[1]. However, Fig.5 shows two resonances similar to Fraenkel[1] but the resonance at 18.90ppm shows no coupling, even with resolution enhancement.

Thornton[7] and Delong[4] showed that by adding n-propanol to [n-propyllithium]=2M with an O:Li ratio of 0.2, there were new resonances at 16.55ppm and 18.15ppm at 193K. Both were very broad resonances. Ellington[6] showed similar results with an O:Li ratio of 0.04, there were new resonances at 16.50ppm and 18.10ppm at 183K.

Before the addition of n-propanol, Ellington[6], Delong[4] and Thornton[7] did not see the additional resonances upfield 18.4ppm. Only after the addition of n-propanol was there evidence for additional resonances. In Ellington[6] and Delong's[4] spectra the two additional nonamer resonances were at 19.3ppm and 20.2ppm at 193K.

Thornton's[7] spectrum shows an additional resonance at 67.2ppm. Due to the c1 carbon bonded to the oxygen

$$\begin{array}{ccccc} & & c1 & c2 & c3 \\ Li\text{-}O\text{-} & & CH_2\text{-} & CH_2\text{-} & CH_3 \end{array}$$

This resonance is seen with any ratio of O:Li. There are no resonances near 67ppm in Figure 5, therefore there is apparently no $LiOCH_2CH_2CH_3$.

Figure 5 shows the ^{13}C NMR spectrum. Several new resonances are present downfield from 15.80ppm compared to the room temperature spectrum. There are six resonances in the inset. Four resonances appear at 15.80ppm, 17.60ppm 18.65ppm and 18.90ppm. These are the c1 carbons from four of the five aggregates reported by Fraenkel.[1] Table 3 compares the resonances in Hertz referenced to Fraenkel's hexamer and coupling constants. Figure 5 still show small broad resonances at 18.00ppm and 18.11ppm. The resonances 18.00ppm and 18.11ppm are not due to mixed aggregates with oxygen since there are no resonances present near 67.2ppm. The following table shows other possible structures for 18.00ppm and 18.11ppm to clarify what these resonances might be due to.

Table 4: Propane, Propene, and Hexane Resonances

Propane[8] (ppm)		Propene[8](ppm)			n-hexane[8](ppm)		
c1, c3	c2	c1	c2	c3	c1, c6	c2, c5	c3, c4
15.6	16.1	18.7	133.1	115	13.9	22.9	32.0

These three were referenced in $CDCl_3$ at room temperature and compared to Figures 3 and 5. There is only one resonance similar to propene at 18.7ppm but there are no resonances at 133.1ppm and 115ppm. The resonances at 18.00ppm and 18.11ppm are not due to propane or propene. One possible byproduct may be n-hexane. Two regions match up well at 13.9ppm (c1,c6) and 22.5ppm (c2,c3). The third resonance at 32.0ppm (c3,c4) is close to 30.5ppm.

The c2 and c3 carbon regions for n-propyllithium have additional resonances. These resonances have not been assigned for this temperature. An APT and ^{13}C-^{1}H HETCOR NMR experiments at this temperature could clarify which resonances are associated with c2 and c3 carbons.

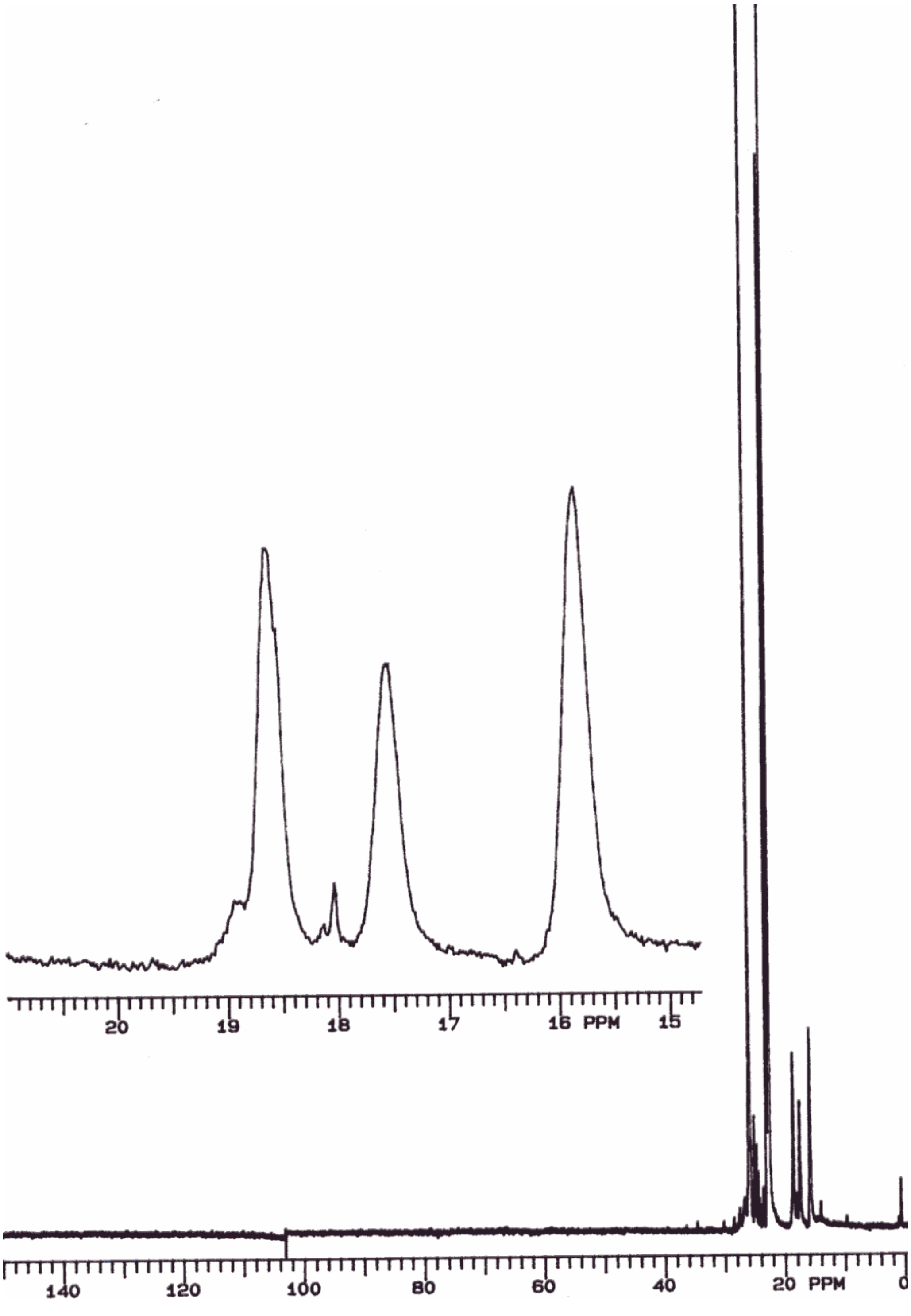

Figure 5– ^{13}C NMR Spectrum of n-propyllithium at 214K. Inset shows expanded c1 regions. 15.80ppm-hexamer, 17.60ppm-octamer, 18.65ppm nonamer, 18.90ppm nonamer aggregates

^{6}Li 1-D NMR Spectra at 214K (Figures 6-7)

The ^{6}Li, ^{1}H coupled (Figure 6) and ^{1}H decoupled (Figure 7) NMR spectra show additional peaks upfield from the hexamer aggregate. Additional peaks occur at -0.09ppm, -0.16ppm, -0.36ppm and -0.41 compared to room temperature. These are consistent with Fraenkel's[1] and Thomas'[2] results. However, Figures 6 and 7 show additional resonances beyond -0.61ppm. The following is a table of all resonances in Figure 7.

Table 5: ^{6}Li NMR Chemical Shifts and Description from Fig. 7

δ^6Li	Aggregate
0	6, broad
-0.09	8, broad
-0.16	9, broad
-0.36	Under investigation, narrow
-0.41	Under investigation, broad
-0.61	Unaccounted, narrow, new
-0.63	Unaccounted, narrow, new
-0.68	Unaccounted, narrow, new
-0.84	Unaccounted, narrow
-0.86	Unaccounted, narrow
-0.98	Unaccounted, narrow, new
-1.11	Unaccounted, narrow

The following table compares results from the current work results with Fraenkel's[1] and Huang's[5] results.

Table 6: ^{6}Li NMR Chemical Shift Results

^{6}Li NMR Chemical Shift Results (ppm)					
Hexamer	Octamer	Nonamer	Nonamer	Nonamer	Reference
0	-0.09	-0.16	-0.36	-0.41	Figure 7, a
0	-0.07	-0.17	-0.37	-0.42	Fraenkel[1], b
0	-0.09	-0.17	Not present	Not present	Huang's[5], c

(a)[n-Pr^{6}Li]=2M at 44 MHz
(b)[n-Pr^{6}Li]=0.6M at 39.73 MHz
(c)[n-Pr^{6}Li]=2M at 44 MHz

Huang[5] used ^{13}C-^{6}Li HETCOR NMR experiment to correlate the ^{13}C NMR c-1 resonances to the ^{6}Li NMR resonances. This experiment was performed at 193K. The ^{13}C resonance at 15.6ppm was coupled to the ^{6}Li resonance at 0ppm, the hexamer aggregate. The ^{13}C resonance at 17.4ppm was coupled to the ^{6}Li resonance at -0.09ppm, the octamer aggregate. The ^{13}C resonance at 18.5ppm was coupled to the ^{6}Li resonance at -0.17ppm, the major nonamer aggregate. Delong[4] showed similar results with a ^{13}C-^{6}Li HETCOR.

Further upfield in the ^{6}Li{^{1}H} NMR spectrum, Figure 7, are resonances at -0.36ppm and -0.41ppm. Fraenkel[1] showed that these resonances were additional nonamer aggregates from the coupling constants of ^{13}C NMR spectra and integration of the ^{13}C and ^{6}Li resonances. Huang's[5] ^{6}Li{^{1}H} NMR spectrum does not show the additional resonances at -0.36ppm and -0.41ppm.

Ellington's[6] $^{6}Li\{^{1}H\}$ NMR spectrum shows the two resonances -0.36ppm and -0.41ppm only after the addition of n-propanol, O:Li=0.04, with three additional resonances at -0.51ppm, -1.13ppm and -2.02ppm. Ellington's[6] resonance at –1.13ppm is similar to this work's resonance at –1.11ppm. The resonance at –2.02ppm corresponds to the lithium bonded to the oxygen resonance.

$$^{6}Li\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

Any addition of oxygen into the n-propyllithium system results in a new resonance at –2.02ppm below 220K. Both Figures 6 and 7 show no addition of oxygen at 214K. The ^{6}Li resonances at -0.36ppm and -0.41ppm are not due to oxygen.

The following is a table of Figure 7 and Huang's[5] hydride region.

Table 7: ^{6}Li NMR Chemical Shifts for Hydrides

Figure 7		Huang[5]	
$\delta^{6}Li$	Coupling(Hz)	$\delta^{6}Li$	Coupling(Hz)
-0.61	N/a	N/a	N/a
-0.63	N/a	N/a	N/a
-0.68	N/a	-0.68	1.4
N/a	N/a	-0.75	N/a
-0.84	N/a	-0.85	N/a
-0.86	N/a	-0.86	N/a
-0.98	0.8	N/a	N/a
-1.11	0.9	N/a	N/a

Huang's[5] n-propyllithium ^{6}Li NMR spectra showed a hydride resonance at -0.68ppm with $J_{^6Li-^1H}$=1.4Hz at 214K. There were three additional resonances at -0.75ppm, -0.85ppm and -0.86ppm. Two of the three resonances are similar to the ones seen in Figure 7 at –0.84ppm and –0.86ppm. Huang's[5] spectrum shows no resonance at –2.02ppm.

Several resonances collapsed to single resonances in Figure 7, with ^{1}H decoupling. All resonances are considered to be hydrides since the resonances collapsed to thinner peaks. These resonances are not present at 204K and below. This suggests that these resonances are hydrides. There are four new resonances reported at –0.61ppm, -0.63ppm, -0.68ppm, -0.98ppm. All are considered to be hydride aggregates. The couplings for two resonances were -1.11ppm, $J_{^6Li-^1H}$=0.9Hz, and -0.98ppm, $J_{^6Li-^1H}$=0.8Hz. The additional resonances (-0.61ppm, -0.63ppm, -0.68ppm, -0.84ppm, -0.86ppm) were not resolved enough to determine coupling constants.

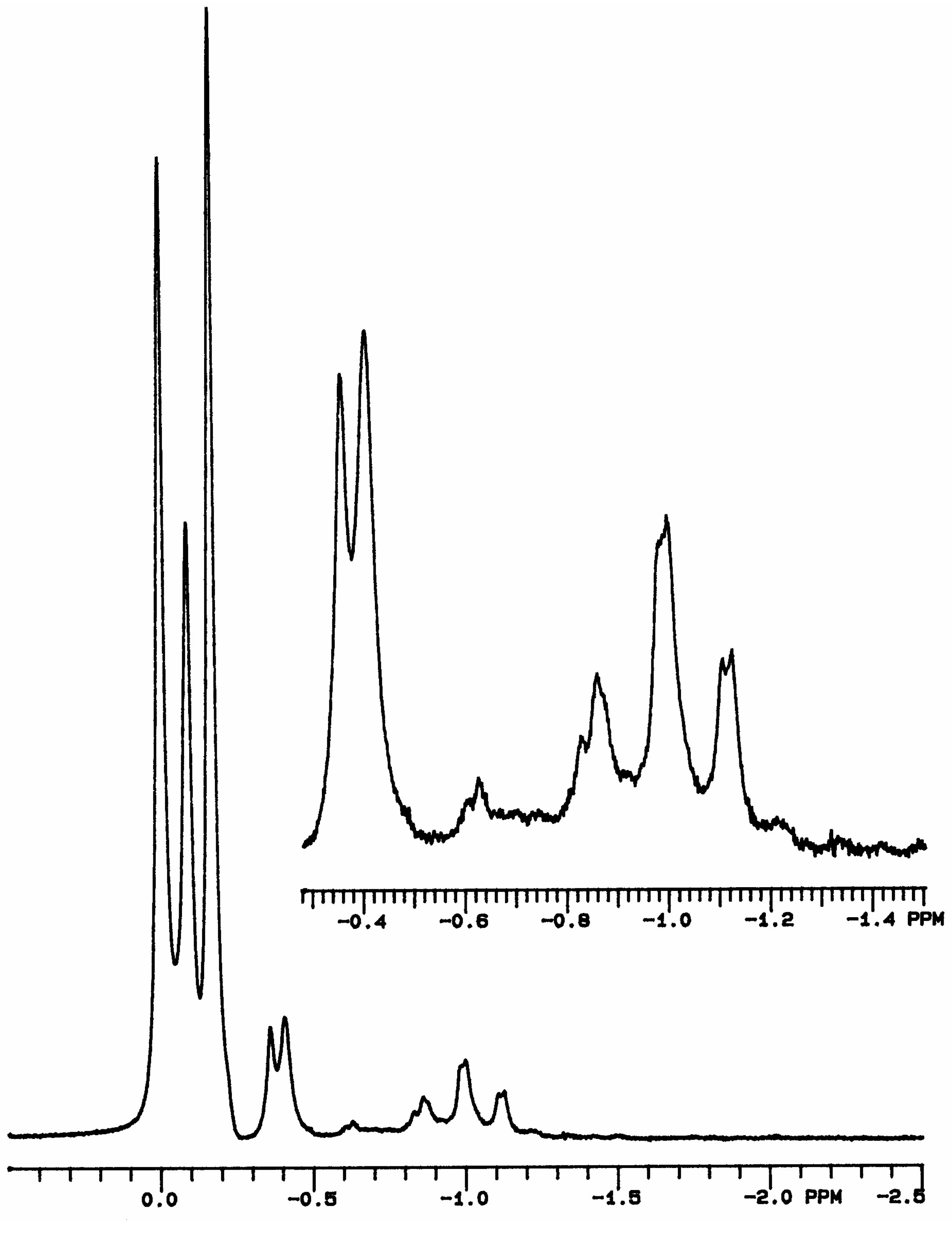

Figure 6– ^{6}Li NMR Spectrum of n-propyllithium at 214K. ^{1}H coupled (DM=N). Peaks at 0.0ppm, hexamer; -0.09ppm, octamer; -0.16ppm, nonamer. Peaks at –0.36ppm and –0.41ppm unaccounted. Inset shows expanded lithium hydride region.

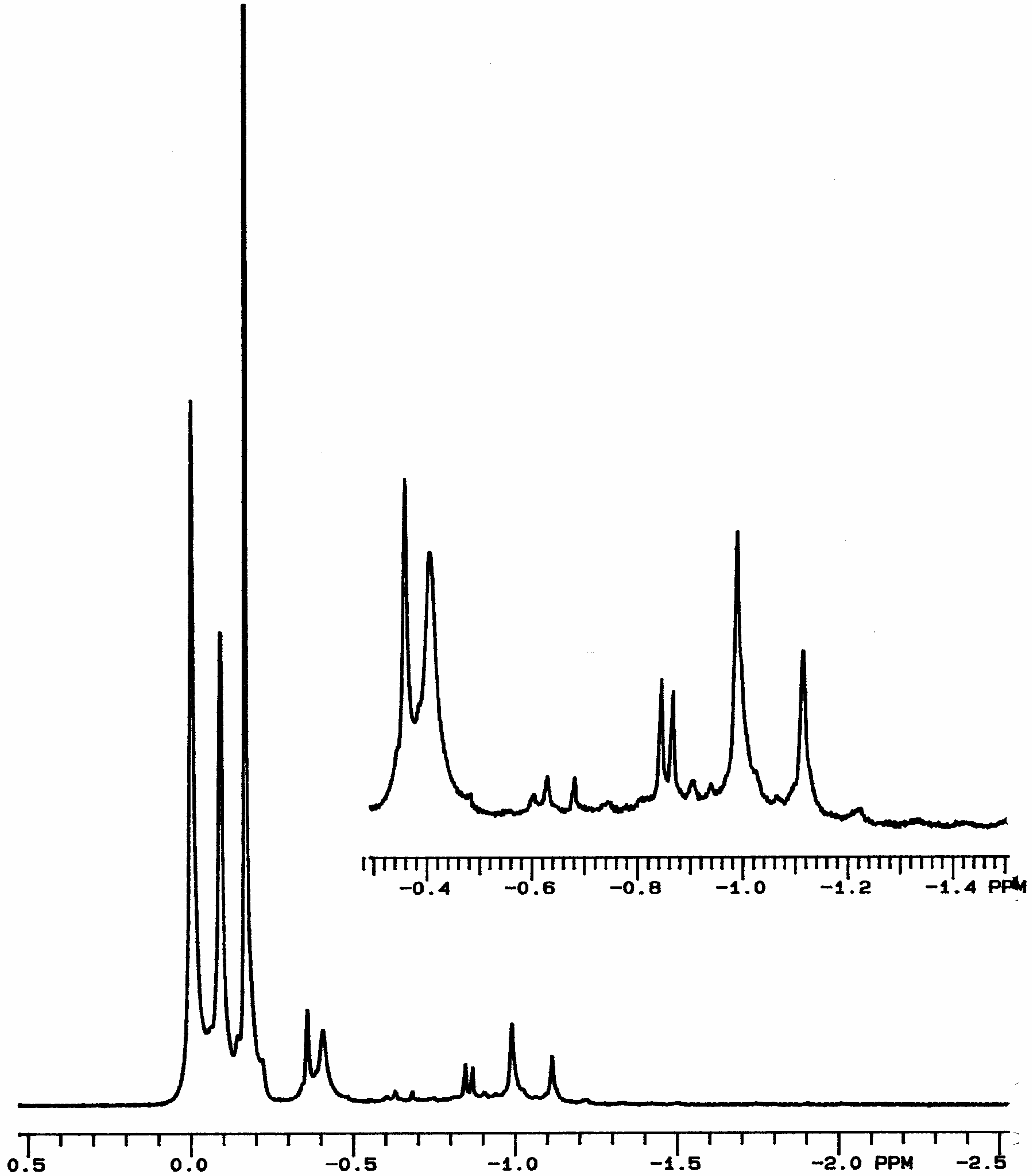

Figure 7– ^{6}Li{^{1}H} NMR Spectrum of n-propyllithium at 214K. ^{1}H decoupled (DM=NNY). Peaks at 0.0ppm, hexamer; -0.09ppm, octamer; -0.16ppm, nonamer. Peaks at –0.36ppm and –0.41ppm unaccounted. Inset shows

expanded lithium hydride region. All peaks have collapsed to singlets in hydride region.

$^{13}C\{^6Li, ^1H\}$ 1-D NMR Spectra at 214K (Figures 11-15)

There were additional experiments performed to clarify the unassigned lithium aggregates. The following figures show a completely decoupled $^{13}C\{^6Li, ^1H\}$ 1-D spectrum and selectively decoupled $^{13}C\{^6Li, ^1H\}$ 1-D spectra. The inset for Figure 5 shows the $^{13}C\{^1H\}$ without ^6Li decoupling. Note the broad resonance due to the unresolved ^{13}C-^6Li coupling. When the ^6Li decoupler was set to decouple all ^6Li peaks all ^{13}C c1 resonances collapsed (Figure 8 and Table 8). There are six resonances observed with ^6Li decoupling. These resonances include 15.80ppm(hexamer), 17.60ppm(octamer), 17.65ppm, 18.44ppm, 18.65ppm(nonamer) and 18.90ppm. The resonances 17.65ppm, 18.44ppm, 18.90ppm were buried under larger resonances. The resonances at 18.00ppm and 18.11ppm did not collapse. Since these resonances did not collapse, then 18.00ppm and 18.11ppm are not coupled to any ^6Li nuclei.

The ^6Li decoupler was adjusted to only decouple the ^6Li resonance at –0.16ppm (Figure 9 and Table 8), the major nonamer aggregate. This clarifies which ^{13}C nuclei are coupled to these ^6Li nuclei. Figure 9 shows the ^{13}C c1 region. Resonances 15.80ppm, hexamer, and 17.60ppm, octamer, are broad. The resonances at 18.44ppm and 18.65ppm collapsed to narrower peaks. This suggests that the decoupler is attenuated enough to only decouple the ^6Li nuclei at -0.16ppm, the major nonamer aggregate. There is a new additional peak at 18.73ppm. The resonance at 18.90ppm is broad.

Next, the ^6Li decoupler was set to decouple the ^6Li resonance at -0.36ppm (Figure 10 and Table 8), a minor nonamer aggregate. The ^{13}C c1 resonance at 18.90ppm collapsed (Figure 10). The ^{13}C c1 resonances at 15.80ppm(hexamer), 17.60ppm(octamer) and 18.65ppm(nonamer) are broad. Next, the ^{6}Li decoupler was set to decouple the ^{6}Li resonance at -0.41ppm, another minor nonamer aggregate. Nothing collapsed in the ^{13}C c1 region.

Table 8: ^{13}C{^{6}Li, ^{1}H} NMR Chemical Shifts with ^{6}Li Decoupler Set at Specified Resonance for Fig. 8-10

Figure 5		All ^{6}Li resonances decoupled		^{6}Li decoupler set to -0.16ppm		^{6}Li decoupler set to -0.36ppm	
δ ^{13}C	Analysis	δ ^{13}C	Analysis	δ ^{13}C	Analysis	δ ^{13}C	Analysis
15.80	6, broad	15.80	6, narrow	15.80	6, broad	15.80	6, broad
17.60	8, broad	17.60	8, narrow	17.60	8, broad	17.60	8, broad
		17.65	New, n/a	17.65	Buried	17.65	Buried
18.00	broad	18.00	broad	18.00	broad	18.00	broad
18.11	broad	18.11	broad	18.11	broad	18.11	broad
		18.44	narrow	18.44	narrow	18.44	hidden
18.65	9, broad	18.65	9, narrow	18.65	9, narrow	18.65	9, broad
				18.73	New, n/a		
18.90	9, broad	18.90	9, narrow	18.90	9, broad	18.90	9, narrow

Then, the ^{6}Li decoupler was adjusted to the ^{6}Li resonance at -0.99ppm. All ^{13}C c1 resonances collapse (Figure 11 and Table 9). This is considered a hydride region. The ^{6}Li decoupler was then adjusted to the resonance at -1.12ppm. Many resonances collapsed for the ^{6}Li resonance at -1.12ppm (Figure 12 and Table 9).

Table 9: $^{13}C\{^{6}Li, ^{1}H\}$ NMR Chemical Shifts with ^{6}Li Decoupler Set at Specified Resonance for Fig. 11 and 12

Figure 5		^{6}Li decoupler set to –0.99ppm		^{6}Li decoupler set to –1.12ppm	
δ ^{13}C	Description	δ ^{13}C	Description	δ ^{13}C	Description
15.80	6, broad	15.80	6, narrow	15.80	6, narrow
17.60	8, broad	17.60	8, narrow	17.60	8, narrow
		17.65	new, n/a	17.65	new, n/a
18.00	broad	18.00	broad	18.00	broad
18.11	broad	18.11	broad	18.11	broad
		18.44	narrow	18.44	narrow
18.65	9, broad	18.65	9, narrow	18.65	9, narrow
		18.73	not present	18.73	not present
18.90	9, broad	18.90	9, narrow	18.90	9, narrow

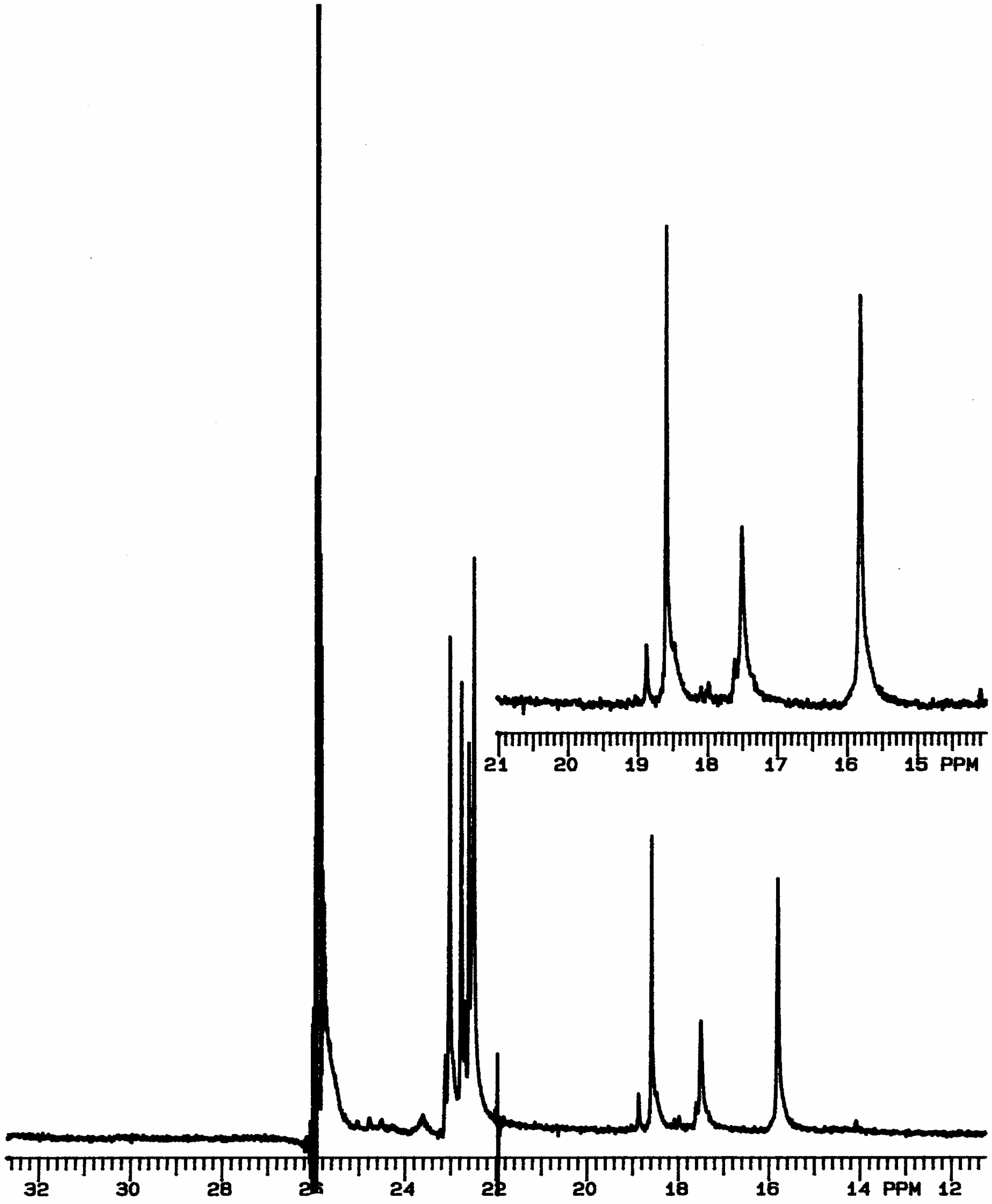

Figure 8– 1-D $^{13}C\{^6Li, ^1H\}$ NMR Spectrum of n-propyllithium at 214K. The ^6Li decoupler position was set to 34,140,804.4Hz. This is the ^6Li peak at –0.16ppm. The attenuator was set to 0. The watt-meter was set to 15W. This decoupled all ^6Li peaks. Inset contains the c1 region. Reported peaks at 15.80ppm, hexamer; 17.60ppm, octamer; 18.65ppm, nonamer; 18.90ppm, nonamer. Unaccounted peaks at 17.65ppm and 18.44ppm.

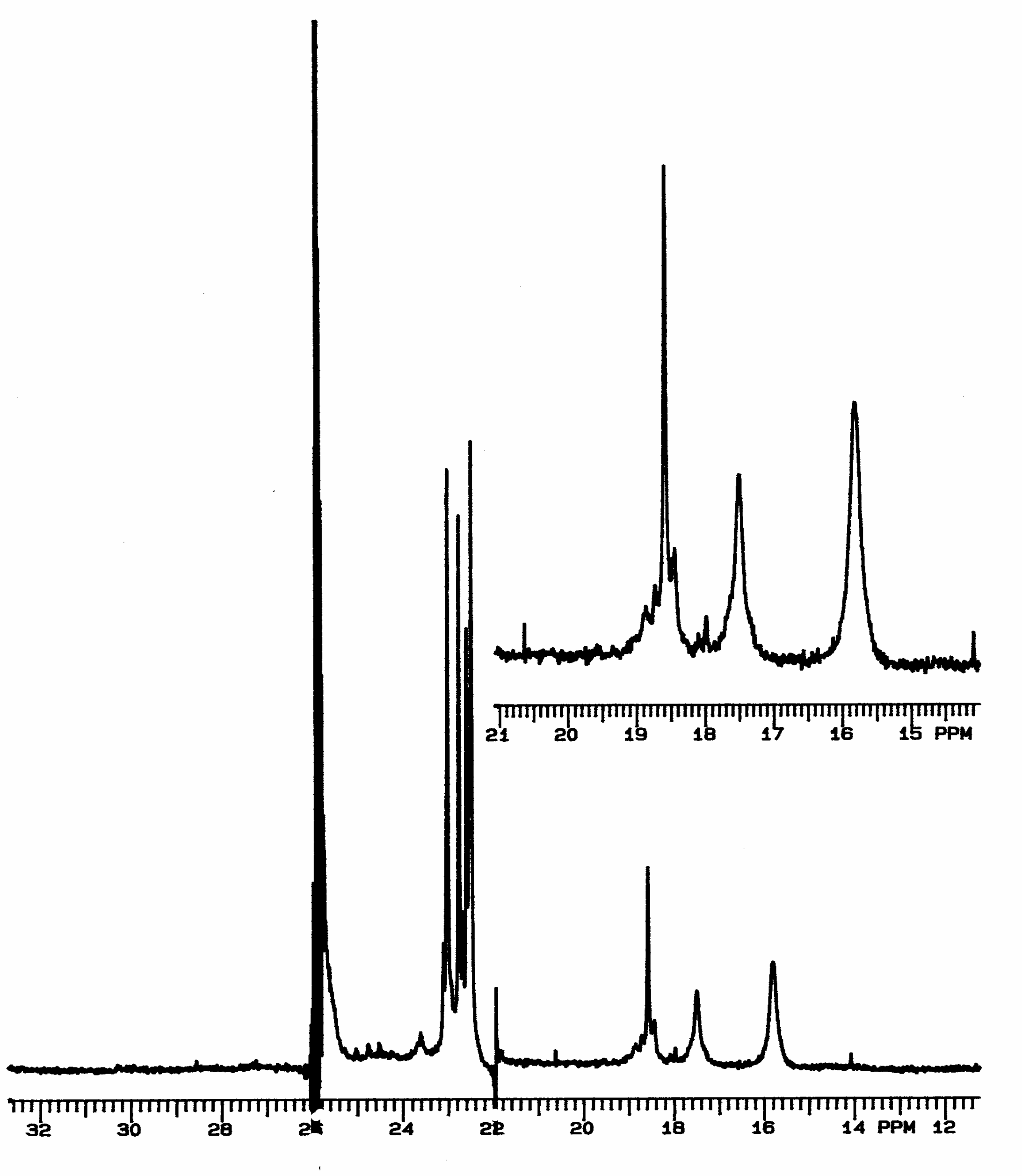

Figure 9– 1-D $^{13}C\{^{6}Li, ^{1}H\}$ NMR Spectrum of n-propyllithium at 214K. The ^{6}Li decoupler position was set to 34,140,804.4Hz. This is the ^{6}Li peak at –0.16ppm. The attenuator was set to 04. The watt-meter was set to 5W. This decoupled only the ^{6}Li peak at –0.16ppm. Inset contains the c1 region. Reported peaks at 15.80ppm, hexamer (broad); 17.60ppm, octamer (broad); 18.65ppm, nonamer (collapsed); 18.90ppm, nonamer (broad). Unaccounted peaks at 18.44ppm and 18.73ppm (collapsed).

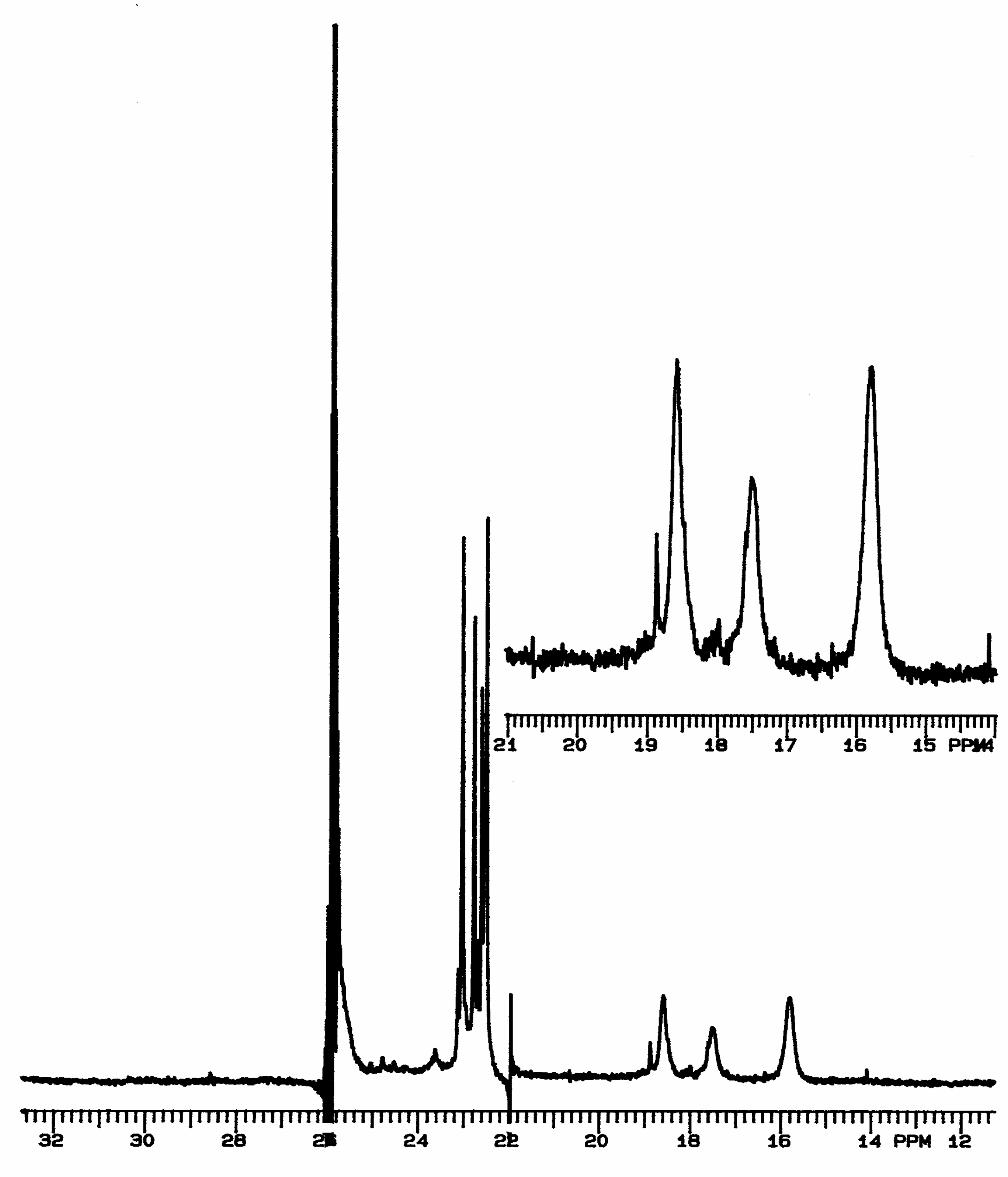

Figure 10– 1-D $^{13}C\{^{6}Li, {}^{1}H\}$ NMR Spectrum of n-propyllithium at 214K. The ^{6}Li decoupler position was set to 34,140,795.8Hz. This is the ^{6}Li peak at –0.36ppm. The attenuator was set to 04. The watt-meter was set to 5W. This decoupled only the ^{6}Li peak at –0.36ppm. Inset contains the c1 region. Reported peaks at 15.80ppm, hexamer (broad); 17.60ppm, octamer (broad); 18.65ppm, nonamer (broad); 18.90ppm, nonamer (collapsed). Unaccounted peaks at 18.44ppm and 17.65ppm (collapsed).

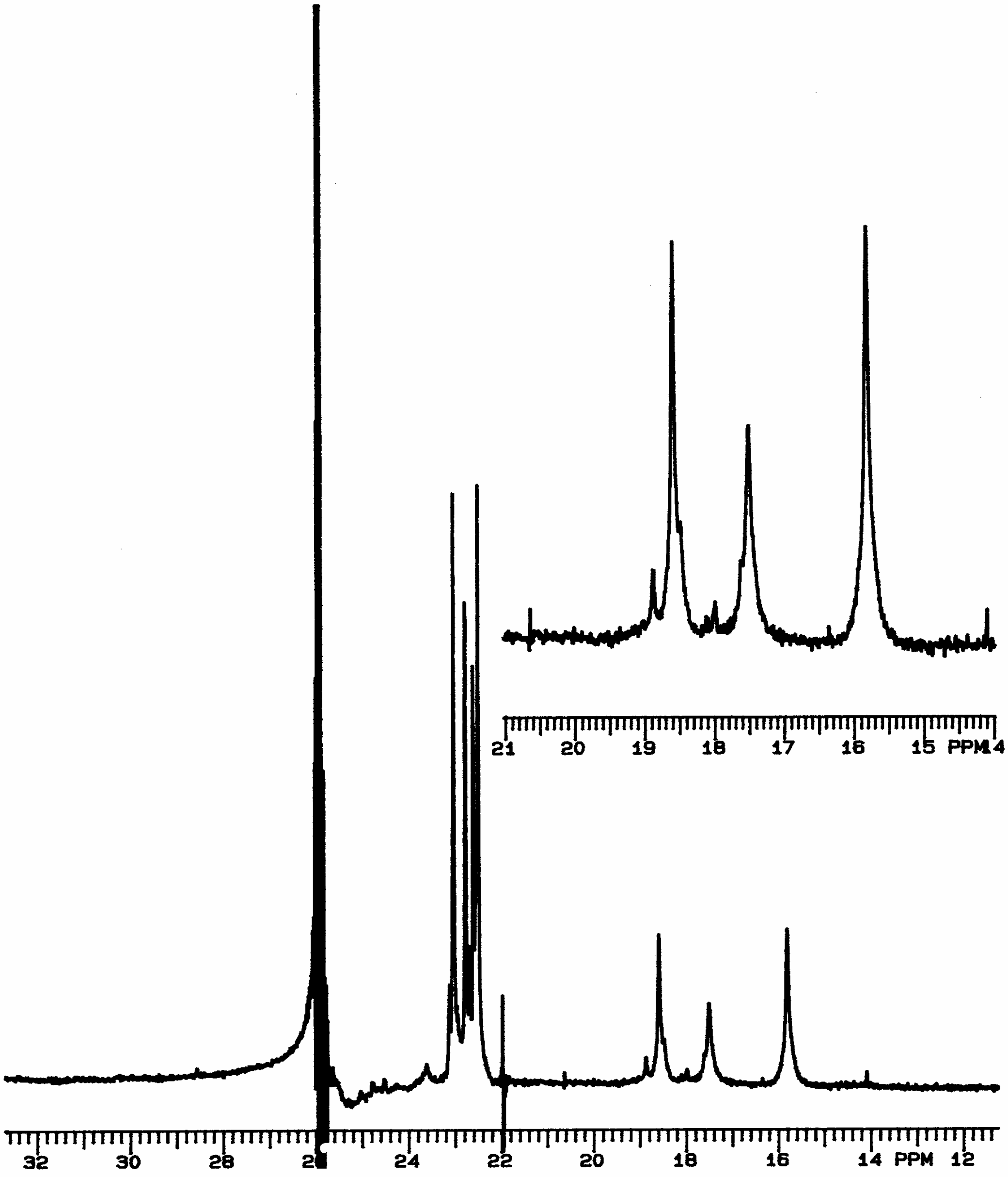

Figure 11– 1-D $^{13}C\{^{6}Li, ^{1}H\}$ NMR Spectrum of n-propyllithium at 214K. The ^{6}Li decoupler position was set to 34,140,768.2Hz. This is the ^{6}Li peak at –0.99ppm. The attenuator was set to 04. The watt-meter was set to 5W. This decoupled only the ^{6}Li peak at –0.99ppm. Inset contains the c1 region. All c1 peaks collapsed.

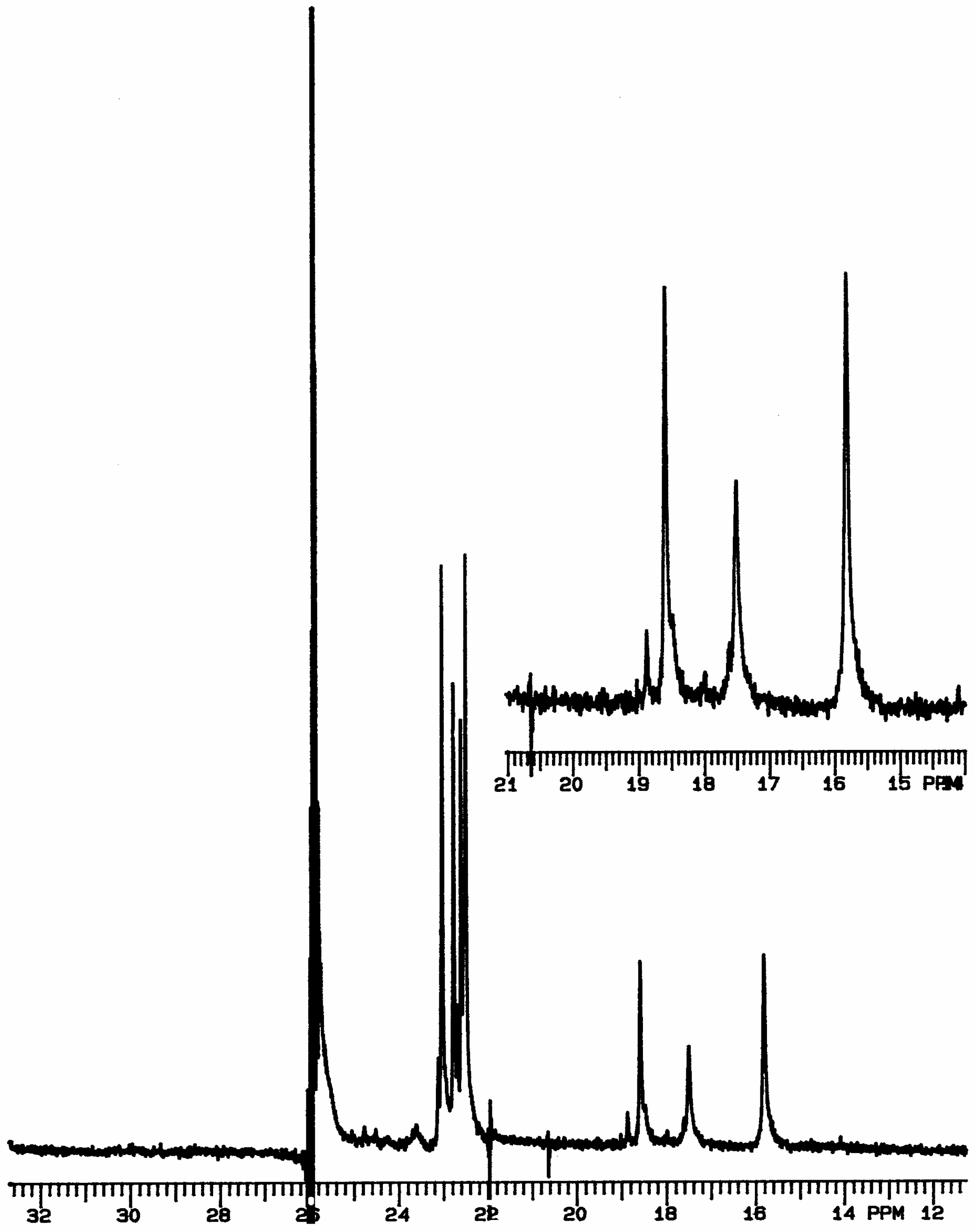

Figure 12– 1-D $^{13}C\{^{6}Li, ^{1}H\}$ NMR Spectrum of n-propyllithium at 214K. The ^{6}Li decoupler position was set to 34,140,762.5Hz. This is the ^{6}Li peak at –1.11ppm. The attenuator was set to 04. The watt-meter was set to 5W. This decoupled only the ^{6}Li peak at –1.11ppm. Inset contains the c1 region. All c1 peaks collapsed.

Summary of n-PrLi at 214K

The ^{13}C NMR spectrum at 214K, Figure 5, contain the hexamer, octamer and major nonamer aggregates reported by Fraenkel.[1] The ^{6}Li NMR spectra at 214K, Figure 6 and 7, contain the five resonances reported by Fraenkel[1] with additional upfield resonances.

The ^{6}Li selectively decoupled ^{13}C NMR spectra at 214K, Figures 8-12, show which ^{6}Li resonances are coupled to the ^{13}C c1 resonances. The completely decoupled ^{13}C{^{6}Li, ^{1}H} spectrum shows three additional peaks. One at 17.61ppm was buried under the octamer peak. The peaks 18.47ppm and 18.87ppm were both buried under the major nonamer aggregate. Decoupling only the ^{6}Li resonance for the major nonamer at -0.16ppm shows collapsed resonances in the ^{13}C{^{6}Li, ^{1}H} NMR spectrum, Figure 9, at 18.44ppm, new, 18.59ppm, nonamer, and 18.73ppm, new.

Decoupling the ^{6}Li resonance at -0.36ppm, the upfield minor nonamer, shows collapsed resonances in the ^{13}C{^{6}Li, ^{1}H} NMR spectrum, Figure 10, at 17.61ppm,new, and 18.87ppm, nonamer. Decoupling the ^{6}Li resonance at -0.41ppm shows no collapsed resonances in the ^{13}C{^{6}Li, ^{1}H} NMR spectrum. The decoupling at the ^{6}Li resonances at -0.99ppm, Figure 11, or -1.12ppm, Figure 12, collapsed all c1 peaks in the ^{13}C{^{6}Li, ^{1}H} NMR spectrum.

Conclusion of n-PrLi at 214K

The ^{13}C{^{6}Li, ^{1}H} NMR spectra at 214K, Figures 8-12, show that the minor nonamer at –0.36ppm in the ^{6}Li NMR spectrum is coupled to the ^{13}C resonance at 18.90ppm. This is consistent with Fraenkel's[1] assignments. However the other ^{6}Li resonance that Fraenkel[1] assigned to a minor nonamer, at –0.41ppm does not couple to any ^{13}C resonances.

Typically hydrides are formed with the addition of oxygen as an alkoxide. This is accomplished with the use of an alcohol. Many of the references point this out with additional resonances near 67ppm in the ^{13}C NMR spectrum. The ^{13}C and ^{6}Li NMR spectra show that no oxygen was present in this system. However there were numerous hydride resonances. This may be due to the small n-propyl group allowing for beta-hydride elimination.

The data presented shows two lithium hydride aggregates coupled to all n-propyllithium aggregates. Evidence for this are the numerous ^{13}C{^{6}Li, ^{1}H} selective decoupling and ^{6}Li 1D NMR resonances. The most interesting results were from the ^{13}C{^{6}Li, ^{1}H} 1-D NMR spectra at 214K where the ^{6}Li decoupler was set to the hydride resonances at -0.99ppm and -1.12ppm in the ^{6}Li NMR spectrum. This study suggests there are several lithium hydride/n-propyllithium mixed aggregates. This suggests that the major peaks contain hydrides if the coupling is coming from the hydrides. This raises the question of where these hydrides are coming from. One possibility could be from the alkyl protons. The next step would be to run a ^{6}Li-^{1}H HETCOR.

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