THE ANALYSIS OF PROPELLANT MATERIALS BY FOURIER TRANSFORM NMR

Final Report

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PROPELLANT ANALYSIS CARBON-13 NMR NUCLEAR MAGNETIC RESONANCE

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20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

This research was undertaken to investigate the suitability of high-resolution proton and carbon-13 Fourier transform NMR spectroscopy for the qualitative and quantitative analysis of compounds of the type used in propellant formulations. Materials studied include polymers, plasticizers, aromatic nitro compounds, aliphatic nitrate esters, carboranes, stabilizers, and related materials. It was found that NMR analysis is of great utility in the chemical analysis of propellant ingredients, particularly carbon-13 NMR, both for qualitative and quantitative analysis.

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Introduction. The purpose of this research was to investigate the suitability of high-resolution ^1H and ^{13}C Fourier transform nuclear magnetic resonance spectroscopy for the qualitative and quantitative analysis of compounds of the type used in propellant formulations for solid-fueled rocket motors. The use of NMR in propellant analysis is not new; however, until recent years its low sensitivity limited its applications primarily to ^1H analysis of rather concentrated solutions. The recent availability of pulsed Fourier transform NMR instrumentation opened new possibilities for analysis, owing to the much greater sensitivity, relative to continuous wave NMR. This higher level of sensitivity is still not as great as that realized in gas chromatographic/mass spectrometric analysis, but NMR has the advantage of being applicable to non-volatile- as well as volatile substances. Furthermore, it provides more useful information for compound identification than mass spectrometry.

Proton NMR has been used for several years in propellant analysis; in this report we show that with Fourier transform NMR the utility is even greater. We also show that carbon-13 NMR can be extremely useful for both qualitative and quantitative analysis of mixtures of the type found in propellant formulations.

^{1}H NMR Studies. Proton NMR experiments were performed to demonstrate the greater sensitivity of Fourier transform NMR (FTNMR) relative to continuous wave NMR. In principle, the greater inherent sensitivity of FTNMR has two applications in proton work, analysis of small samples, and analysis of minor constituents of larger samples. We have found that samples as small of 0.5 mg can be routinely analyzed by FTNMR. For example, 0.5 mg of p-nitrotoluene gives a readily identifiable spectrum. This level of sensitivity, coupled with the type of information contained in a typical proton spectrum, makes FTNMR competitive with mass spectrometry for the qualitative analysis of unknown substances available in small amounts. The second application, the analysis of minor constituents of mixtures, continues to be difficult, even with the greater sensitivity of FTNMR. A modern spectrometer with a good data system ought to show a dynamic range of at least 4,000, meaning that constituents of 0.1% composition ought to be detectable. However, we were never able to realize this level of resolution; indeed, we have difficulty in detecting components below 1%. In addition to instrumentation problems, there is the more fundamental difficulty that ^{13}C satellites of the major constituents, impurities in the solvent, etc., give peaks which seriously interfere with the analysis.

A problem which has long plagued ^{1}H NMR mixture analysis is the rather narrow spread of proton absorption frequencies. Quite often, signals from different molecules overlap to such an extent that analysis is impossible. The use of chemical shift reagents such as tris(dipivalomethanato)europium often causes large changes in chemical shifts, resulting in a greater spread of absorption frequencies, and hence a greater chance that signals from different molecules will be separated from each other. We therefore undertook a study to determine the feasibility of using chemical shift reagents to facilitate mixture analysis by ^1H NMR. Isomeric nitrotoluenes were mixed with both tris(dipivalomethanato)europium, (Eu(dpm)$_3$), and tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium, Eu(fod)$_3$, in order to determine if these reagents would indeed induce shifts in the proton frequencies. Unfortunately, neither of these reagents had any significant effect on the spectra. Data are shown in Table 1 for the effect of Eu(fod)$_3$ on four nitrotoluenes.

Table 1

Effect of Eu(fod)$_3$ on ^1H Chemical Shifts in Four Nitrotoluenes[a]

Compound	Chemical Shifts[b] Without Eu(fod)$_3$	With Eu(fod)$_3$[c]	Proton Type
2,4-Dinitrotoluene	2.77	2.78	CH_3
	8.82	8.89	H-3
	8.36	8.40	H-5
	7.60	7.62	H-6
3,5-Dinitrotoluene	2.67	2.66	CH_3
	8.38	8.42	H-2
	8.85	8.92	H-4
2,4,5-Trinitrotoluene	2.80	2.80	CH_3
	8.60	8.63	H-3
	7.87	7.88	H-6
2,4,6-Trinitrotoluene	2.74	2.74	CH_3
	8.83	8.86	H-3

[a] 5% solutions in $CDCl_3$. [b] ppm, downfield from TMS. [c] 0.3 mole Eu(fod)$_3$ per mole nitrotoluene.

The data in Table 1 for 2,4-dinitrotoluene and 3,5-dinitrotoluene show clearly the problem of overlapping ^1H signals. A small amount of the latter compound would be completely hidden by a larger amount of the former. Unfortunately, the use of chemical shift reagents does not help separate the peaks.

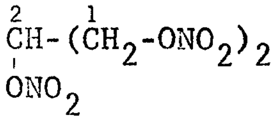
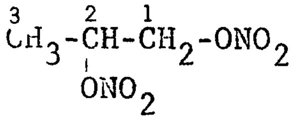
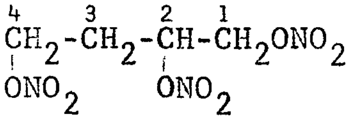
In conclusion, it has been demonstrated that FTNMR allows for the analysis of solutions which are more dilute by an order of magnitude than was possible with continuous wave techniques. However, the analysis of minor constituents (less than 1%) in a mixture is almost as difficult with FTNMR as with continuous wave NMR. Overlapping peaks in nitrotoluene mixtures could not be resolved by the addition of chemical shift reagents.

^{13}C NMR Studies. The majority of our effort was devoted to ^{13}C research. For the purpose of this report the research can be divided into four major areas: characterization of aliphatic nitrate esters, characterization of nitrotoluenes and analysis of mixtures, characterization of miscellaneous compounds found in propellant formulations, and structural studies of polybutadienes. Each of these will be discussed below.

Characterization of Aliphatic Nitrate Esters. Spectral analysis of six of the more common aliphatic nitrate esters has been completed. Compounds studied include nitroglycerin, 1,2-propylene glycol dinitrate, diethylene glycol dinitrate, triethylene glycol dinitrate, 1,2,4-butanetriol trinitrate, and trimethylolethane trinitrate. The structural formulas and ^{13}C chemical shifts are shown in Table 2. The spectral assignments were made with the help of proton-coupled spectra, off-resonance decoupled spectra, and ^{13}C/^{1}H chemical shift cross-correlation. Note that the overall

Table 2

^{13}C Chemical Shifts of Aliphatic Nitrates[a]

Compound	δ_1[b]	δ_2	δ_3	δ_4
 $\underset{ONO_2}{\overset{2}{C}H}-(\overset{1}{C}H_2-ONO_2)_2$	68.19	74.81		
 $\overset{3}{C}H_3-\underset{ONO_2}{\overset{2}{C}H}-\overset{1}{C}H_2-ONO_2$	71.99	76.07	15.03	
 $\underset{ONO_2}{\overset{4}{C}H_2}-\overset{3}{C}H_2-\underset{ONO_2}{\overset{2}{C}H}-\overset{1}{C}H_2ONO_2$	67.89	70.86	27.24	53.57
$\overset{3}{C}H_3-\overset{2}{C}-(\overset{1}{C}H_2-ONO_2)_3$	72.81	38.53	17.17	
$O-(\overset{2}{C}H_2-\overset{1}{C}H_2-ONO_2)_2$	72.03	67.41		
$(\overset{3}{C}H_2-O-\overset{2}{C}H_2-\overset{1}{C}H_2-ONO_2)_2$	72.20	67.28	70.80	

[a] In $CDCl_3$ [b] ppm, downfield from TMS

$\Delta\delta$ in these compounds is about 60 ppm, whereas in the proton spectra it is only about 4 ppm. Clearly ^{13}C NMR shows considerable promise for analysis of mixtures of these materials.

It should also be pointed out that the presence of chemicals such as plasticizers and stabilizers does not significantly hamper the analysis of these compounds. The chemical shifts of these materials, which are tabulated in a later section of this report, do not significantly overlap with those of the nitrate esters.

Characterization of Nitrotoluenes. All six of the dinitrotoluenes and four of the trinitrotoluenes have been analyzed by ^{13}C NMR. Using a variety of techniques, such as analysis of proton-coupled spectra and off-resonance proton decoupling, the spectral assignments shown in Table 3 were made. Most of the measurements were made in chloroform; DMSO and acetone were used only in cases of very low solubility. One of the most difficult compounds to analyze was 2,3,5-trinitrotoluene, owing to its instability in DMSO and its lack of solubility in chloroform. The data in Table 3 for this compound is the result of 100,000 scans of a dilute solution in chloroform. The only signals detected were those of the protonated carbons. In general, the nonprotonated carbons were difficult to detect, owing to their longer relaxation times and smaller nuclear Overhauser effect. Quadrupolar broadening by ^{14}N further hampered efforts to assign the nitrogen-bearing carbons. It should be noted that the chemical shifts (reported in Table 3) are somewhat sensitive to solvent. The chemical shifts in DMSO are up to 1 ppm less than the corresponding shifts in chloroform.

Table 3

^{13}C Chemical Shifts of Nitrotoluenes[a]

Compound	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_{CH_3}
2,3-dinitrotoluene	132.63	----	----	123.16	130.44	137.12	17.23
2,4-dinitrotoluene	140.70	149.54[b]	120.19	147.14[b]	126.99	134.08	20.63
2,5-dinitrotoluene	135.17	152.53	125.59	122.07	149.25	127.65	20.02
2,6-dinitrotoluene	127.60	151.56	127.59	127.75	127.59	151.56	14.74
3,4-dinitrotoluene	145.97	125.30	137.68	143.39	125.16	133.54	21.36
3,5-dinitrotoluene	142.46	129.22	149.11	116.30	149.11	129.22	20.07
2,3,4-trinitrotoluene[c]	140.16	----[d]	----[d]	----[d]	128.19	136.78	18.21
2,4,6-trinitrotoluene	134.28	151.68	122.31	145.73	122.31	151.68	15.65
2,4,5-trinitrotoluene[e]	141.61	----	122.40	----	----	129.56	20.56
2,3,5-trinitrotoluene	----	----	----	118.94	----	131.53	17.60

[a] ppm, downfield from tetramethylsilane, in $CDCl_3$ unless otherwise noted.

[b] These values may be transposed

[c] in DMSO

[d] Assignment uncertain, either 139.2 ppm or 138.5 ppm

[e] in $CDCl_3$/acetone

The usefulness of ^{13}C analysis of mixtures of these materials is readily apparent. The chemical shifts of the various carbon atoms are spread over a very wide frequency range, relative to the proton shifts in the same molecules. Specifically, note that the methyl carbons are spread over about 7 ppm and the aromatic carbons over about 35 ppm, whereas in the ^{1}H spectra the corresponding signals are found over ranges of only 0.2 ppm and 1.5 ppm respectively.

The mixtures shown in Table 4 were prepared in order to test the accuracy of ^{13}C NMR analysis. Spectra were measured and integrated intensities of signals from protonated carbons were then used to determine the composition of the mixtures. The assumption was made that these carbons will all have essentially the same relative response factors (i.e., essentially the same relaxation times and nuclear Overhauser effect). It is clear from examination of the results that the compounds are not only being identified in the mixture, but also determined quantitatively with a reasonable degree of accuracy. The speed of the analysis, the positive

Table 4

^{13}C Analysis of Nitrotoluene Mixtures

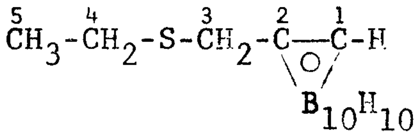
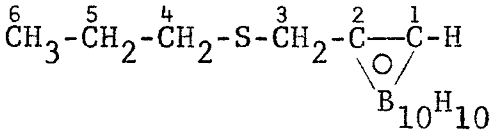
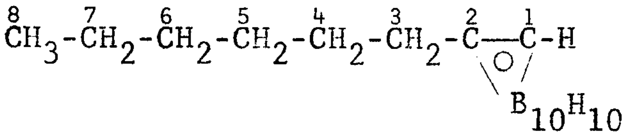
	Composition		^{13}C Results	
Compound	Mixture 1	Mixture 2	Mixture 1	Mixture 2
2,4,6-Trinitrotoluene	88%(312 mg)	68.5%(332 mg)	87.0%	71.6%
2,4,5-Trinitrotoluene	1.6%(5.6 mg)	3.7%(18.1 mg)	2.0%	3.8%
2,6-Dinitrotoluene	4.2%(11.8 mg)	10.3%(40.1 mg)	4.4%	8.3%
2,4-Dinitrotoluene	4.0%(11.5 mg)	10.6%(41.4 mg)	4.4%	9.2%
2,5-Dinitrotoluene	2.2%(6.4 mg)	6.8%(26.5 mg)	2.1%	6.5%

identification of components, and the quantitative nature of the results together illustrate the tremendous utility of ^{13}C FTNMR. No other analytical technique offers a better combination of speed, positive identification, and quantitation.

Characterization of Miscellaneous Propellant Ingredients. Tables 5-7 contain spectral data for a number of compounds of interest in propellant formulations. Some of these are used in double base propellants, and others are used in composite propellants. In virtually every case the carbon spectra are of much greater value than the proton spectra in propellant analysis, both because the greater spread in frequencies results in less overlap of spectra of different compounds, and because the spectra are better fingerprints of the compounds than are the proton spectra.

Table 5

^{13}C Chemical Shifts of Three Carboranes[a]

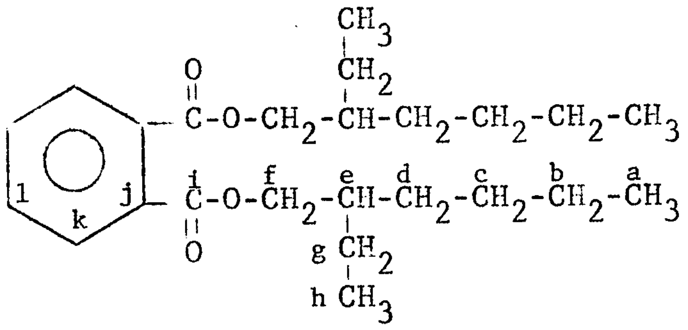
Carboranylmethylethylsulfide	δ_1 = 75.11	δ_2 = 59.82	δ_3 = 38.83
 $\overset{5}{C}H_3-\overset{4}{C}H_2-S-\overset{3}{C}H_2-\overset{2}{C}-\overset{1}{C}-H$ $B_{10}H_{10}$	δ_4 = 28.76	δ_5 = 14.68	
Carboranylmethylpropyl sulfide	δ_1 = 74.84	δ_2 = 59.60	δ_3 = 38.93
 $\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{C}H_2-S-\overset{3}{C}H_2-\overset{2}{C}-\overset{1}{C}-H$ $B_{10}H_{10}$	δ_4 = 36.50	δ_5 = 22.76	δ_6 = 13.25
n-Hexylcarborane	δ_1 = 76.08	δ_2 = 61.40	δ_3 = 38.47
 $\overset{8}{C}H_3-\overset{7}{C}H_2-\overset{6}{C}H_2-\overset{5}{C}H_2-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{2}{C}-\overset{1}{C}-H$ $B_{10}H_{10}$	δ_4 = 31.67[b]	δ_5 = 29.61[b]	δ_6 = 29.00[b]
	δ_7 = 22.81	δ_8 = 14.32	

[a] ppm, downfield from TMS; $CDCl_3$ solvent. [b] Assignments uncertain

Table 6

^{13}C Chemical Shifts of Some Esters[a]

2-Ethylhexyl phthalate



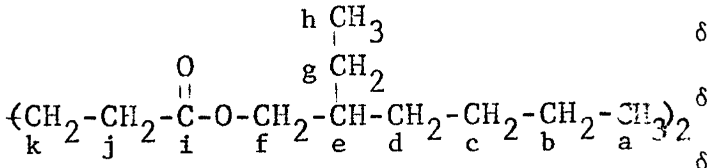
$\delta_a = 14.14$ $\delta_b = 23.09$ $\delta_c = 29.03$

$\delta_d = 30.49$ $\delta_e = 38.86$ $\delta_f = 67.98$

$\delta_g = 23.87$ $\delta_h = 11.01$ $\delta_i = 167.63$

$\delta_j = 132.60$ $\delta_k = 128.84^b$ $\delta_l = 130.93^b$

2-Ethylhexyl adipate



$(\underset{k}{CH_2}-\underset{j}{CH_2}-\underset{i}{\overset{O}{\overset{\|}{C}}}-O-\underset{f}{CH_2}-\underset{e}{\overset{h\,CH_3}{\overset{|}{\overset{g\,CH_2}{\overset{|}{CH}}}}}-\underset{d}{CH_2}-\underset{c}{CH_2}-\underset{b}{CH_2}-\underset{a}{CH_3})_2$

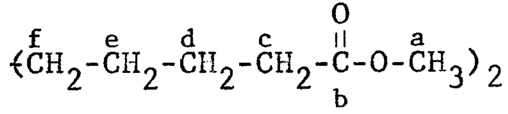
$\delta_a = 14.11$ $\delta_b = 23.09$ $\delta_c = 29.06$

$\delta_d = 30.55$ $\delta_e = 38.89$ $\delta_f = 66.68$

$\delta_g = 23.90$ $\delta_h = 11.04$ $\delta_i = 173.31$

$\delta_j = 34.01$ $\delta_k = 24.57$

Methyl sebacate

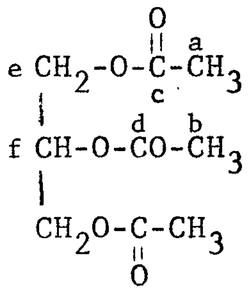


$(\overset{f}{CH_2}-\overset{e}{CH_2}-\overset{d}{CH_2}-\overset{c}{CH_2}-\underset{b}{\overset{O}{\overset{\|}{C}}}-O-\overset{a}{CH_3})_2$

$\delta_a = 51.33$ $\delta_b = 174.07$ $\delta_c = 34.10$

$\delta_d = 25.03$ $\delta_e = 29.21$ $\delta_f = 29.21$

Triacetin



$\delta_a = 20.66$ $\delta_b = 20.84$ $\delta_c = 170.45$

$\delta_d = 170.06$ $\delta_e = 62.28$ $\delta_f = 69.10$

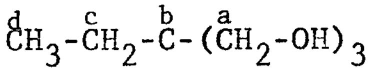
---

[a] ppm, downfield from TMS: $CDCl_3$ solvent. [b] Assignments may be reversed.

Table 7

^{13}C Chemical Shifts of Some Miscellaneous Compounds[a]

1,1,1-Trimethylol propane[b]

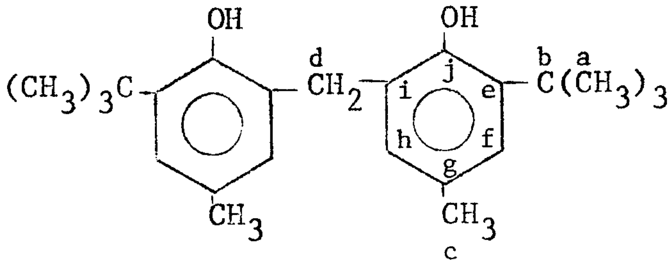


$\overset{d}{C}H_3-\overset{c}{C}H_2-\overset{b}{C}-(\overset{a}{C}H_2-OH)_3$

δ_a = 61.78 δ_b = 43.02 δ_c = 21.08

δ_d = 7.18

2,2'-methylene-bis(4-methyl-6-t-butyl phenol)



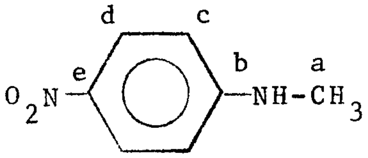
δ_a = 29.9 δ_b = 34.3 δ_c = 20.8

δ_d = 32.2 δ_e = 129.6 δ_f = 126.3

δ_g = 126.6 δ_h = 128.7 δ_i = 136.0

δ_j = 150.0

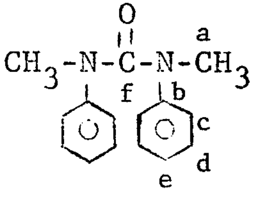
N-Methyl-p-nitroaniline[b]



δ_a = 29.21 δ_b = 155.35 δ_c = 100.45

δ_d = 126.26 δ_e = 135.75

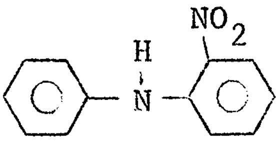
Methyl centralite



δ_a = 39.28 δ_b = 145.55 δ_c = 125.68

δ_d = 128.56 δ_e = 124.77 δ_f = 161.0

2-Nitrodiphenylamine[c]



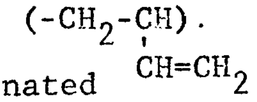
116.03, 117.46, 124.38, 125.65,

126.65, 129.71, 135.63

---

[a] ppm, downfield from TMS, in $CDCl_3$ unless noted. [b] In DMSO-d_6

[c] No assignments were made; shifts reported are for protonated carbons.

Analysis of Polybutadienes by ^{13}C NMR. Polybutadienes of approximately 3000 molecular weight are important in the production of composite propellants. One of the most widely used materials is hydroxy-terminated polybutadiene, a polymer containing both cis- and trans-1,4-units ($-CH_2-CH=CH-CH_2-$) and 1,2-units  ($-CH_2-\underset{CH=CH_2}{\underset{|}{CH}}$). Related materials of interest include carboxy-terminated polybutadiene, and a copolymer of butadiene and acrylic acid.

Proton NMR analysis of these polymers is of very limited utility. Unless extremely high magnetic fields are used, the only information which can be obtained is the ratio of 1,2- to 1,4-addition. In contrast, ^{13}C NMR shows the 1,2- to 1,4-ratio, the cis-1,4 to trans-1,4 ratio, hydroxyl-bearing carbon atoms (in the case of hydroxy-terminated polybutadiene), and considerable information on the polymer microstructure.

The proton-decoupled spectrum of hydroxy-terminated polybutadiene is shown on the next page. The lines fall into three distinct regions: saturated carbons, 24-44 ppm, carbons bearing hydroxyl groups, 63-65 ppm; and unsaturated carbons, 114-145 ppm. Assignment of lines to structural features of the polymer was aided by running proton-coupled spectra and off-resonance decoupled spectra. Also, quantitative chemical shift correlations found in the literature were of considerable value. The assignments are shown in Tables 8 and 9. Analysis indicated that the sample used contained 22% 1,2-units, 53% trans-1,4-units, and 25% cis-1,4-units. Furthermore, both line frequencies and intensities indicated that these units are distributed randomly through the polymer chain. (Note that the experimental intensities agree rather well with intensities calculated on the basis of a random distribution of the three structural units mentioned above.)

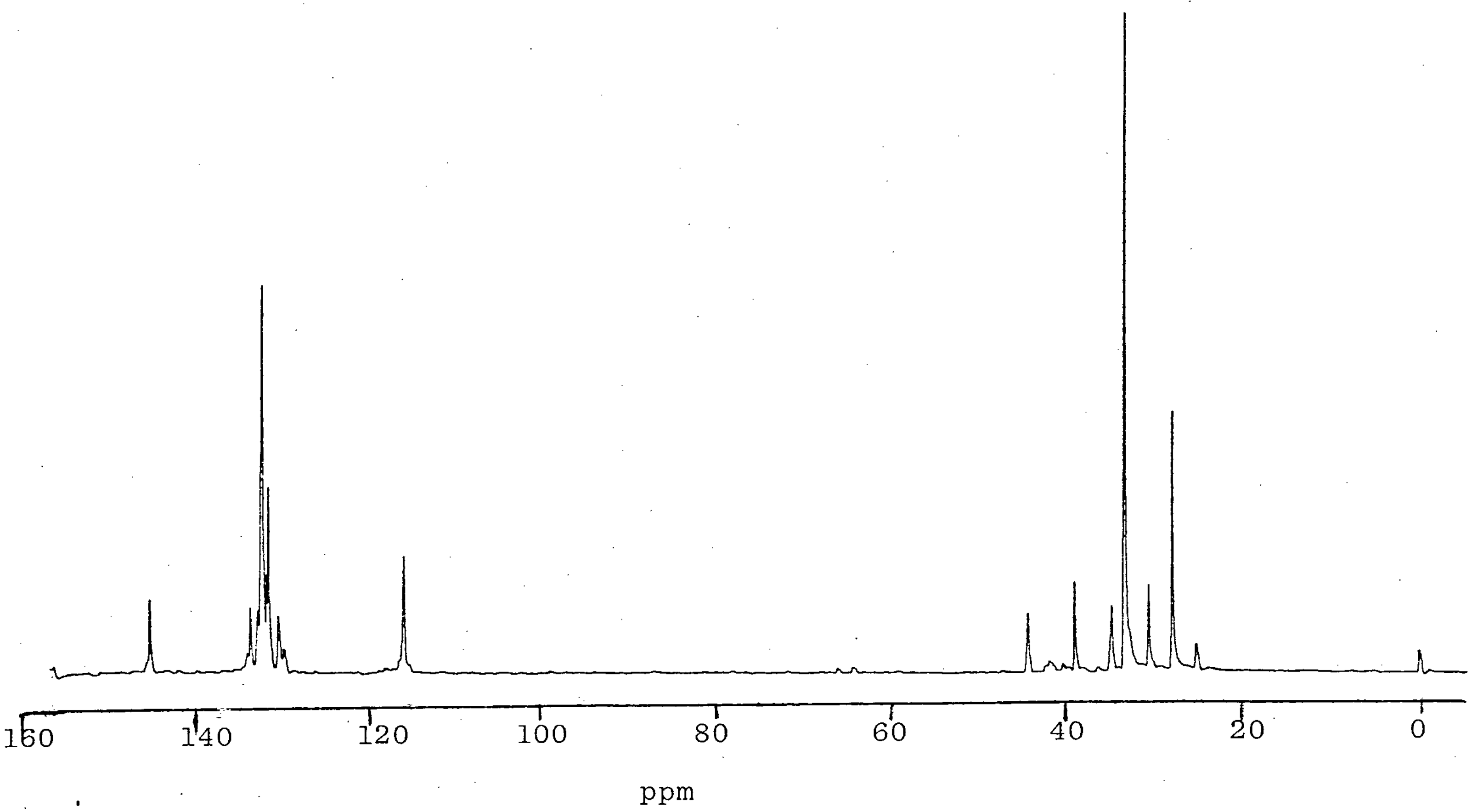
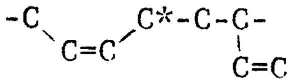
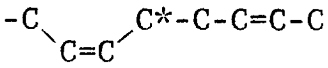
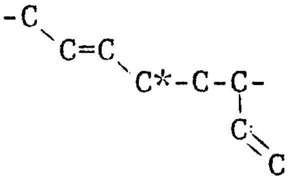
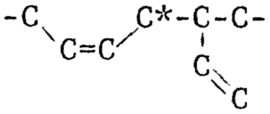
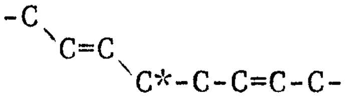
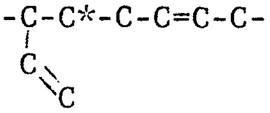
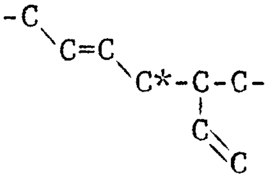
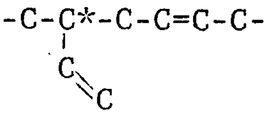


Figure 1. ^{13}C Spectrum of Hydroxy-Terminated Polybutadiene.

Table 8

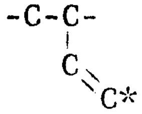
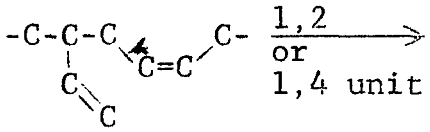
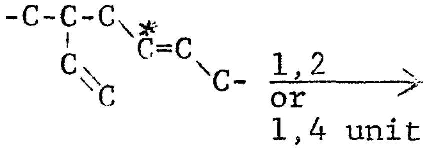
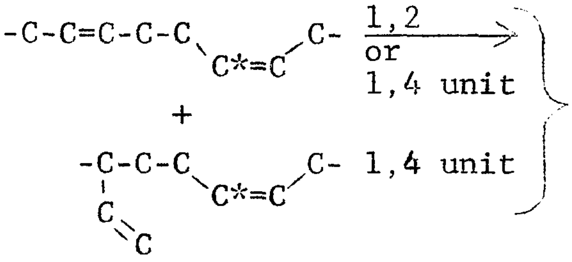
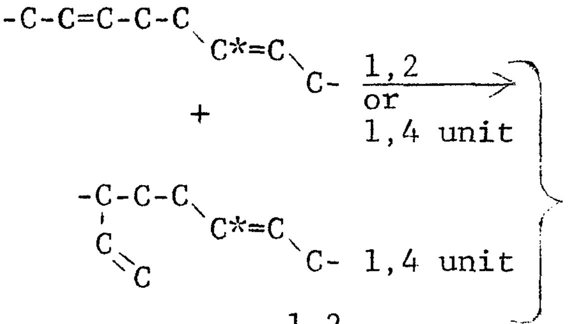
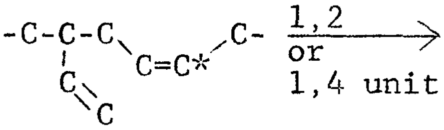
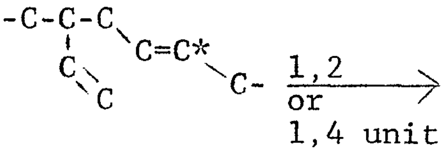
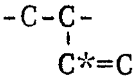
Assignment of Satruated Carbons in Hydroxy-Terminated Polybutadiene

Structure	Chem. Shift (Intensity)[a] Predicted	Found
	24.42 (5.0)	24.85 (5.1)
	27.36 (35.1)	27.41 (35.1)
	30.02 (10.3)	30.02 (8.9)
	31.62 (5.0)	NA[b]
	32.96 (72.7)	32.62 (75.4)
	34-34.5[c] (15.3)	33.98[c] (18.9)
	37.22 (10.3)	38.10 (8.2)
	40.42 (11.9)	43.37 (13.0)

[a] Intensities normalized on peak at 27.41 ppm. [b] Not assigned; may be a shoulder on peak at 32.62 ppm. [c] Two peaks are predicted; observed peak at 33.98 is broad.

Table 9

Assignment of Unsaturated Carbons in Hydroxy-Terminated Polybutadiene

Structure	Chemical Shift (Intensity)	
	Predicted	Found
	114.8	114.1
	128.8 (6.8)	$127.5-127.9^{*a}$ (7.5)
	129.9 (14.1)	$128.0-128.4^{a}$ (12.5)
	130.3 (47.5)	$129.1-129.5^{a,b}$ (48.5)
	131.4 (98.3)	$129.7-130.0^{a}$ (103.3)
	131.8 (6.8)	130.4 (7.0)
	132.9 (14.0)	131.1 (8.0)
	145.3	142.5

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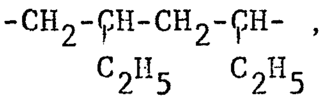
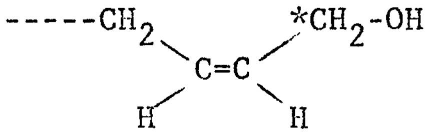
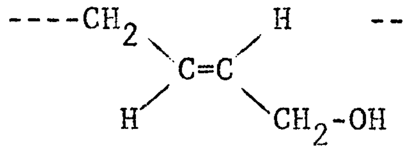
[a] Three lines. [b] Intensities normalized on peak at 129.3 ppm.

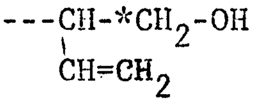
It is interesting to note that lines were found for every combination of 1,2-, cis-1,4-, and trans-1,4- units with the exception of adjacent 1,2 units. This falure is not too surprising in the light of the fact that the probability of occurrence of two of these units side-by-side is rather low. Furthermore, the chemical shift of a particular carbon atom of a 1,2-unit having another 1,2-unit bonded to it is influenced by the other group to which it is bonded such that not one line, but at least three lines result. Consequently, an event of rather low probability is made even more difficult to detect because the signal it gives is not found all in one place. Evidence for the presence of adjacent 1,2-units was obtained by analysis of the hydrogenated polymer. Catalytic hydrogenation removes all the double bonds, making a much simpler structure. The side chain vinylic groups are converted to ethyl groups, resulting in essentially a low molecular weight polyethylene with ethyl branches. Analysis of this material indeed confirmed the presence of the two adjacent ethyl groups  $-CH_2-\underset{\substack{|\\C_2H_5}}{CH}-CH_2-\underset{\substack{|\\C_2H_5}}{CH}-$, along with the much more probable case involving a lone 1,2-unit flanked by 1,4 units.

Examination of Table 9 shows that the lines in the vinylic region fall into eight groups. It is interesting that some of these eight major groupings show fine structure upon close examination. For example, the region between 127.5 and 127.9 ppm shows three lines, presumably due to the triads $\underset{\longrightarrow}{1,2\text{-}C}\diagdown C{=}C\diagup\underset{\longrightarrow}{C\text{-}1,2}$ $\underset{\longrightarrow}{1,2\text{-}C}\diagdown C{=}C\diagup C\text{—trans-1,4}$, and $\underset{\longrightarrow}{1,2\text{-}C}\diagdown C{=}C\diagup C\text{-cis-1,4}$. The three lines between 128.0 and 128.4 can be explained similarly. However, the origin of the fine structure for the 129.1-129.5 and the 129.7-130.0 regions is not so straightforward. In each of these cases, eight triads, each with an unsaturated carbon of the appropriate shift, can be drawn.

Two weak signals at 63.0 and 64.9 ppm presumably correspond to terminal, hydroxyl-bearing, carbon atoms. The most reasonable structures are shown below:







$$\begin{array}{l}---\mathrm{CH}-{}^{*}\mathrm{CH_2}-\mathrm{OH}\\ \quad\mathrm{CH{=}CH_2}\end{array}$$

The fact that two lines are also observed in the spectrum of the hydrogenated polybutadiene would indicate that the two lines in the original polymer are not coming from the first two structures above, for hydrogenation would give only one line, owing to the loss of the cis and trans isomerism.

Two other polymers were studied, carboxy-terminated polybutadiene, and a copolymer of acrylic acid and polybutadiene. These polymers gave spectra very similar in appearance to that of the hydroxy-terminated polybutadiene. The polyurethane rubber which is formed by curing hydroxy-terminated polybutadiene with isophoronodiisocyanate could also be analyzed by ^{13}C NMR. The room temperature spectrum of the rubber was recognizable, and as the temperature was increased to 100°C, the resolution increased until the spectrum was almost as good as that of the original polybutadiene.

This work is of potential value for a number of reasons. In making composite propellants, the fuel and oxidizer are mixed with the polymer and then a difunctional isocyanate is added which reacts with the hydroxyl groups to produce a polyurethane rubber containing the fuel, oxidizer, and any other ingredients added. Different batches of polymer cure at different rates; ^{13}C NMR analysis of the polymer may be able to determine the reason for this behavior. The fact that the solid polymer can be analyzed may make it possible to analyze the propellant itself. This would be very useful in a study of long-term stability of propellants. Problems such as chemical degradation and migration of additives ought to be amenable to study by ^{13}C NMR.

DEGREES AWARDED

Name	Degree	Thesis Title	Present Position
Michael Ku	M.S.*	The Analysis of Propellant Materials by Fourier Transform NMR.	Graduate Student Dept. of Chemistry Purdue University Lafayette, Indiana

*Student has completed all requirements for the M.S., but has not had final oral exam. He will return for the final oral in June 1977.