ERDE 22/M/68

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MINISTRY OF TECHNOLOGY

EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

TECHNICAL MEMORANDUM No. 22/M/68

The NMR Spectra of Nitrate Esters

R.T.M. Fraser

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by

R.T.M. Fraser

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19th December 1968

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CONTENTS

Reference: WAC/190/019

1. SUMMARY

The ^1H spectra of twenty-one nitrate esters have been measured. These were the higher alkyl nitrates, from n-propyl to n-decyl nitrate, as well as iso-propyl and iso-butyl nitrates; ethylene, tri-, tetra-, and pentamethylene dinitrates; 2,2'-oxydiethyl dinitrate (diethylene glycol dinitrate); glycerol 1,3-dinitrate; 2-chlorotrimethylene dinitrate; meso-1,2-dimethylethylene dinitrate; and glycerol 1,2,3- and butane 1,2,4-triyl trinitrates.

A complete analysis of the spectrum was not possible for any of the compounds: a number, like the corresponding fluorides, give deceptively simple spectra. In others the resolution is not sufficient to allow all the NMR parameters to be evaluated. A brief discussion of the parameters which were obtained, and their use in the analysis of mixtures is given.

2. INTRODUCTION

Previous investigations (1) on the NMR spectra of nitrate esters have been limited to the simplest members of the series, ethyl and methyl nitrate. The present work is concerned with the proton spectra of the higher alkyl nitrates, from n-propyl to n-decyl nitrate, as well as iso-propyl and iso-butyl nitrates; ethylene, tri-, tetra-, and pentamethylene dinitrates; 2,2'-oxydiethyl dinitrate (diethylene glycol dinitrate); glycerol 1,3-dinitrate; 2-chlorotrimethylene dinitrate; meso-1,2-dimethylethylene dinitrate; and glycerol 1,2,3- and butane 1,2,4-triyl trinitrates. Interest in these compounds arises from their importance in propellant technology.

3. EXPERIMENTAL

All spectra except that shown in Figure 2 were measured on a Perkin-Elmer R10 spectrometer. Wherever possible the neat liquids were run, using tetramethyl silane as internal reference.

The nitrate esters required in the study were prepared by the action of mixed sulphuric and nitric acids on the corresponding alcohols. Where necessary, the products were distilled under reduced pressures until impurity peaks could no longer be seen in their infrared spectra (2).

4. RESULTS AND DISCUSSION

The NMR spectra of n-hexyl and n-decyl nitrates, characteristic of the C_6 - C_{10} series, are shown in Figure 1. Each contains three regions. A triplet due to the α-CH_2 group is found at low field strengths, and the separation between the peaks gives a measure of the average vicinal coupling constant, $J_{CH_2CH_2}$. At the other end of the spectrum is an ill defined triplet, degraded towards higher fields, arising from the terminal methyl group of the

/molecule; .....

molecule; the position of its central maximum gives the CH_3 chemical shift accurately, although it is difficult to obtain a precise measure of the coupling constant $J_{CH_3CH_2}$ from the spacing within the triplet itself. The remaining resonance arises from the other methylenes present in the nitrate (four and eight CH_2 groups, respectively, in the examples shown): it is broad, but a triplet composed of three broad peaks can be made out on the low field side, arising from the β-CH_2. The centre of this triplet gives a value for the β-hydrogen chemical shift.

The NMR parameters are listed in Table 1. Most of the variations from one member to another are very small, but are not easily accounted for in terms of inductive effects, so that anisotropic or field effects must be important. The various values of the chemical shift for the methyl group and of the $J_{CH_3CH_2}$ coupling constant are similar to others recorded in the literature (3,4), (ethyl iodide: τ_{CH_3} 8.14 ppm, $J_{CH_3CH_2}$ 7.45 cps; ethyl fluoride: τ_{CH_3} 8.76 ppm; *n*-propyl fluoride: τ_{CH_3} 9.0 ppm, $J_{CH_3CH_2}$ 7.45 cps, $J_{CH_2CH_2}$ 6.20 cps).

The chemical shift of the α-proton in *iso*-propyl nitrate is sufficiently different from the others that the region can be used to determine the concentration of straight chain impurities; for example, Figure 2 shows the NMR spectrum of a mixture of *iso*-propyl and ethyl nitrates (96:4), run on the neat liquid.

The spectra of ethylene dinitrate and diethylene glycol dinitrate are not particularly well resolved, but chemical shifts can be determined approximately for the $-CH_2ONO_2$ methylene groups: the difference is large enough to permit the diethylene glycol dinitrate (an AA'BB' system) to be distinguished from ethylene dinitrate (Table 2; Figure 3).

In a similar way, the spectra of the dinitrates of propane 1,3-diol, butane 1,4-diol, and pentane 1,5-diol differ in the chemical shifts between the α and β methylene groups: $J_{\alpha\beta}$ ranges from 2.4 ppm in $O_2NO(CH_2)_3ONO_2$ to 2.65 and finally to 2.8 ppm in $O_2NO(CH_2)_5ONO_2$. Virtual coupling (5,6) is present in the tetramethylene dinitrate, in contrast to the first order triplets displayed in pentamethylene dinitrate.

Figure 4 shows the spectrum of a typical preparation of 1,2-dimethylethylene dinitrate (butane 2,3-diyl dinitrate); a comparison with that of the pure *meso* compound suggests the former is mainly the *dl* isomer, as might be expected (the melting point of the *dl* diol is only 7.6°C, some 15° lower than that of the pure *meso*, so that preferential enrichment of the liquid phase of a commercial mixture of the diol stored at room temperature is quite likely). Both spectra are of the $X_3AA'X'_3$ type: the methyl resonances are essentially doublets, with two lines (separated by $J_{AX} - J_{AX'}$) accounting for half of the total intensity of the group. The resolution is not sufficient to permit an analysis of the fine structure, although this can be done for the methine resonance of the pure *meso* compound. Figure 4 (c) shows the observed spectrum compared with that calculated using $J_{AX} - J_{AX'} = 6.8$ cps, $J_{AX'} = 0$, and $J_{AA'} = 3.0$ cps. Inspection of the methine region in the racemic preparation

/suggests .....

suggests a somewhat larger value of $J_{AA'}$, holds there, so that the spectra resemble those of the butane 2,3-diacetoxy derivatives rather than the dibromo compounds (Refs 7,8; Table 3). Both subspectra are symmetrical about their mid-points.

Although nitroglycerine (glycerol 1,2,3-trinitrate) possesses a molecular symmetry plane, and is thus optically inactive, the plane does not bisect the connecting line of the geminal protons, which are magnetically non-equivalent. As can be seen from Figure 5 (a), the NMR spectrum is complex and of the $X_2AX'_2$ type: it shows close similarities to (for example) the spectrum of triacetin (9). Two closely related compounds are 1-chlorotrimethylene 2,3-diyl dinitrate and 2-chlorotrimethylene 1,3-diyl dinitrate ($Cl.CH_2.CH(ONO_2)CH_2.ONO_2$ and $O_2NOCH_2.CHCl.CH_2.ONO_2$). These have been used in the past (10) in the preparation of samples of glycerol trinitrate in which one ester group is labelled with nitrogen-15. As can be seen (Figure 5, (b) and (c)), their spectra differ considerably; while the 2-chloro compound shows an essentially first order pattern with only a slight splitting of the methine proton resonance, the 1-chloro derivative is an H_2AX_2 system. The isomers can be distinguished one from another by NMR, and both can be identified in admixture with nitroglycerine itself.

5. ACKNOWLEDGEMENTS

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/TABLE 1 .....

TABLE 1

Chemical Shifts and Coupling Constants

nitrate	Chemical Shifts (τ), ppm			Coupling Constants, cps	
	CH_3	β-CH_2	α-CH_2	$J_{CH_3CH_2}$	$J_{CH_2CH_2}$
ethyl	8.72	-	5.49	7.0	-
n-propyl	9.0	-	5.50	6.9	6.4
n-butyl	9.0	-	5.53	6.7	6.1
n-hexyl	9.10	8.29	5.55	-	6.3
n-heptyl	9.10	8.29	5.56	-	6.1
n-octyl	9.10	8.28	5.58	-	6.3
n-nonyl	9.11	8.29	5.58	-	6.3
n-decyl	9.10	8.33	5.50	-	6.3
iso-propyl	8.66	-	4.79[a]	6.4[b]	-
iso-butyl	8.99	-	5.74	6.5[b]	6.5

[a] α-CH

[b] J_{CH_3CH}

/TABLE 2 .....

TABLE 2

Chemical Shifts, ppm

nitrate	CH_3-	-CH_2- or -CH-	-CH_2ONO_2
ethylene di-	-	-	4.95
2,2'-oxydiethyl di-	-	6.16[a]	5.30
trimethylene di-	-	7.71	5.31
tetramethylene di-	-	8.27	5.46
pentamethylene di-	-	8.27	5.46
butane 1,2,4-triyl tri-	8.53	-	4.43[b]
1,2-dimethylethylene di-(meso)	8.57	-	4.61[b]
(dl)	8.53	-	4.65[b]
glycerol 1,2,3-tri-	-	-	4.24[b] 5.06
glycerol 1,3-di-	-	4.3	5.3
2-chlorotrimethylene di-	-	5.58	5.25

[a] $-CH_2-\underline{CH_2}-O$

[b] $-\underline{CH}-ONO_2$

/TABLE 3 .....

TABLE 3

Coupling Constants in Butane 2,3- Derivatives

Butane	$J_{AA'}$	J_{AX}	$J_{AX'}$
dl-dibromo (Ref. 7)	3.03	6.75	+0.02
meso-dibromo (Ref. 7)	6.26	6.48	-0.13
meso-dinitroxy	3.0	6.8	0
meso-diacetoxy (Ref. 7)	3.53	6.63	+0.03
dl-acetoxy (Ref. 7)	5.12	6.51	-0.08

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KEY TO FIGURES

Fig. 1	NMR spectra - *n*-hexyl and *n*-decyl nitrates.
Fig. 2	Ethyl nitrate (b) as an impurity in *iso*-propyl nitrate (a). The α-proton resonance.
Fig. 3	Ethylene dinitrate (a) and diethylene glycol dinitrate (b - b').
Fig. 4	The methine resonances: (a) 1,2-dimethylethylene dinitrate (b) *meso*-1,2-dimethylethylene dinitrate (c) Calculated and observed for *meso*-butane 2,3-diyl dinitrate. Only one half of the spectrum is shown (expanded scales).
Fig. 5	(a) nitroglycerine (glycerol 1,2,3-trinitrate) (b) 1-chlorotrimethylene 2,3-diyl dinitrate (c) 2-chlorotrimethylene 1,3-diyl dinitrate.

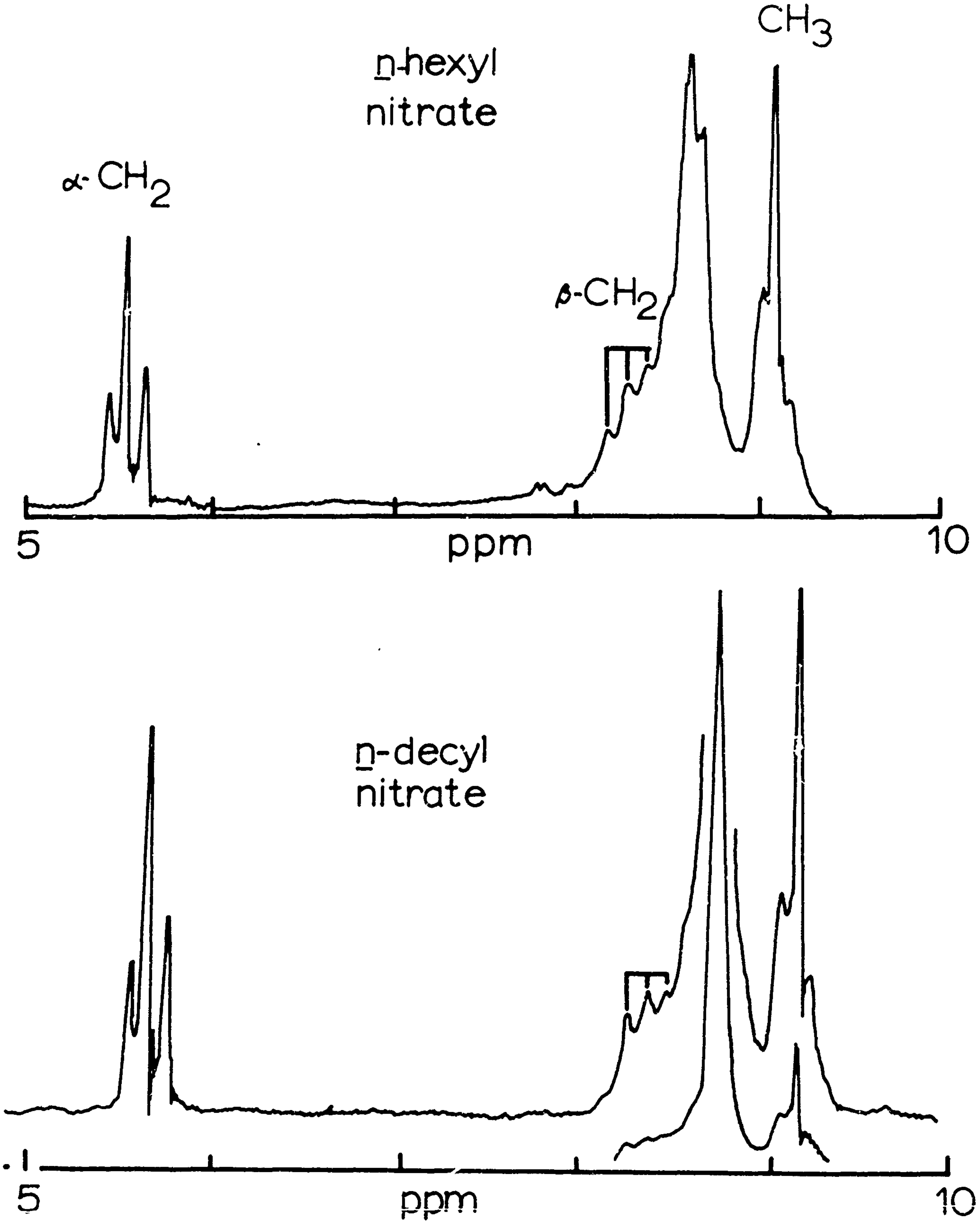

Figure 1

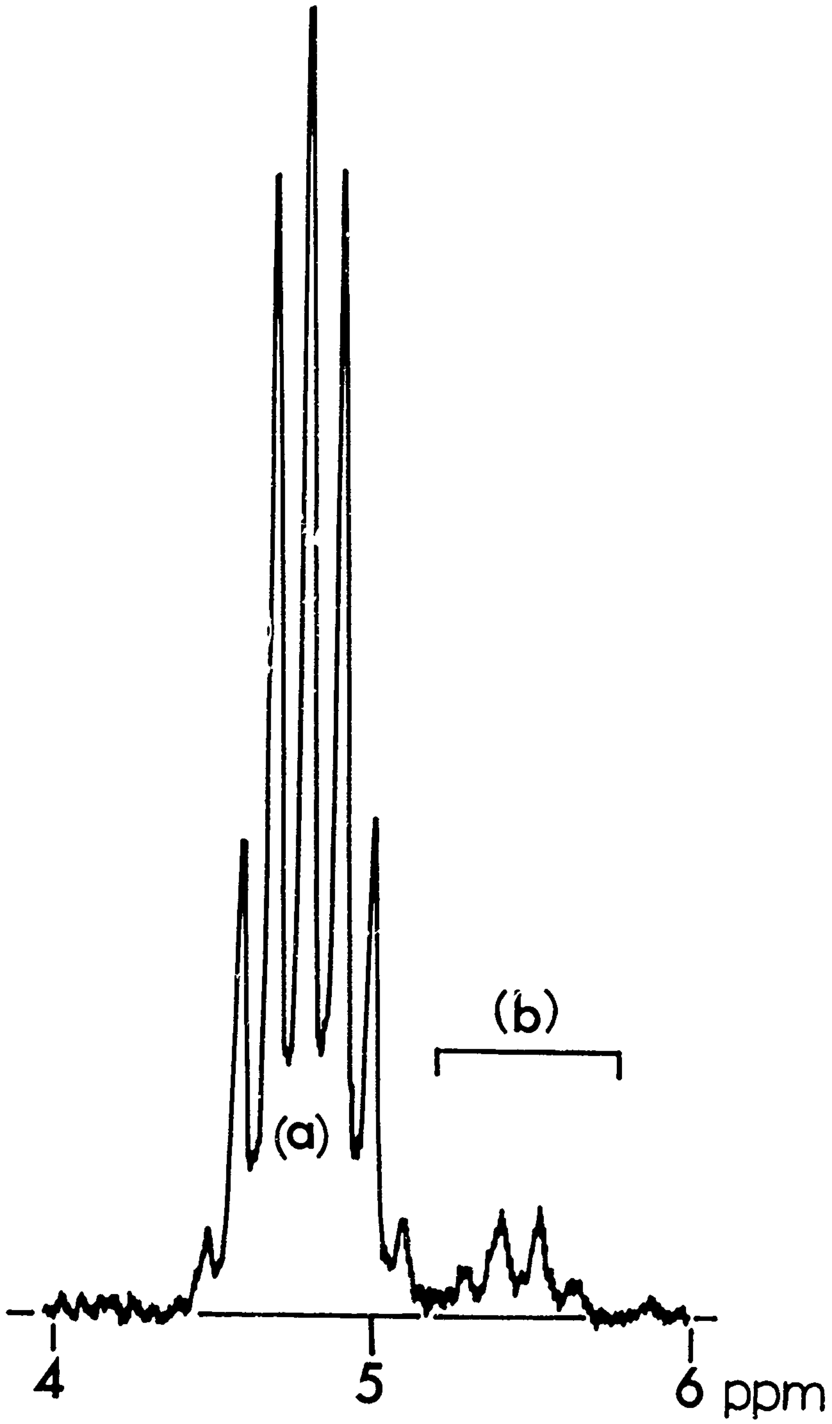

Figure 2

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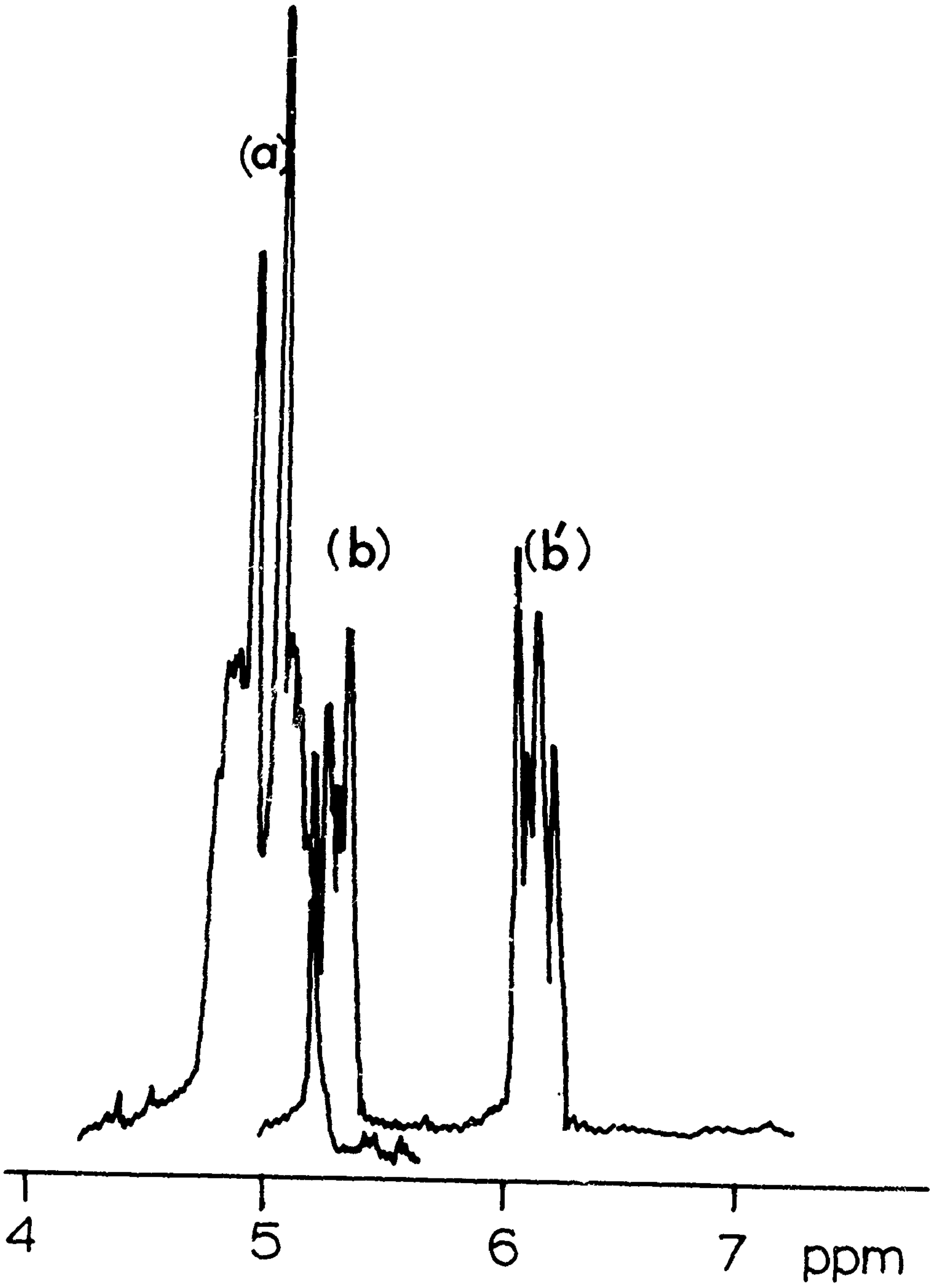

Figure 3

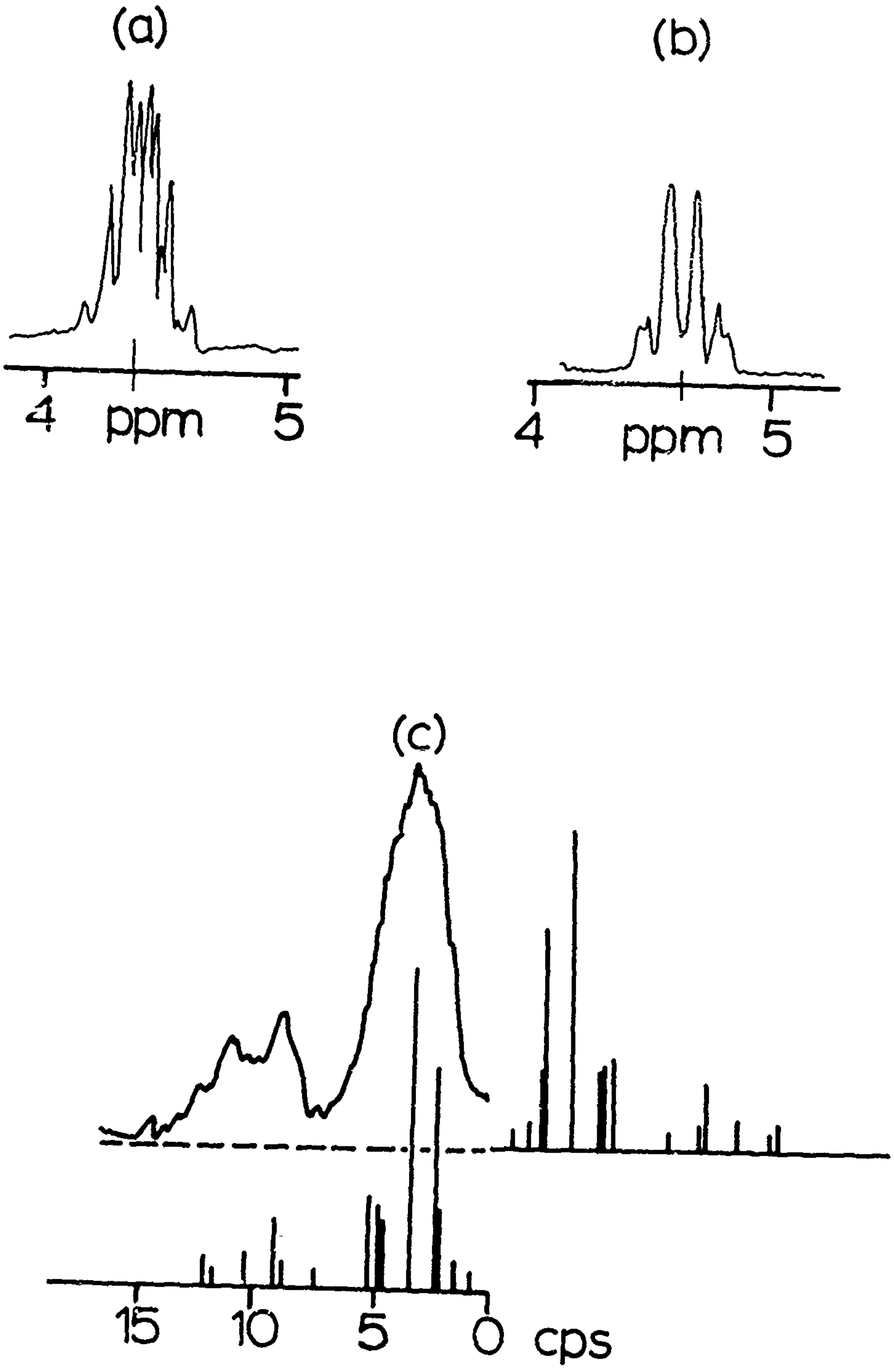

Figure 4

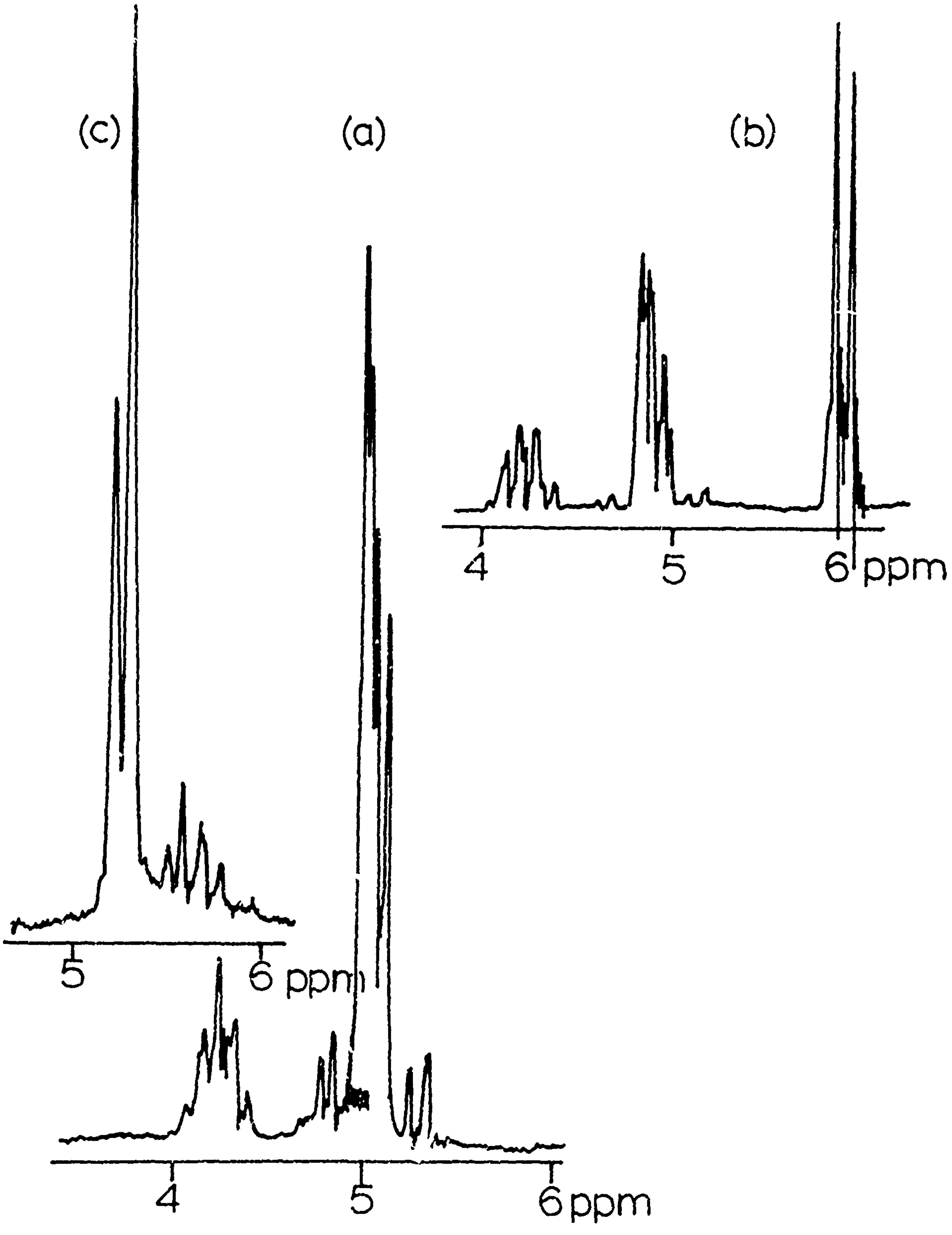

Figure 5

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6 pp, 5 figs, 3 tables

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