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AN INTRODUCTION to NMR SPECTROSCOPY

Bruce Gilbert
Richard Norman

ETSG
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General Editor:
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The University of Aston in Birmingham

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Dr A J G Crawshaw and Mrs Barbara Howard in running the spectra;
Mr John Olive in reproducing the spectra in a form suitable for printing;
Mrs Joyce Poole for preparing the diagrams.

Bruce Gilbert
Richard Norman

1

Topics described on the first side

Principles of nuclear magnetic resonance

Basis of the experimental arrangements

Analysis of ^{1}H n.m.r. spectra:

(a) chemical shifts: their measurement and usefulness in diagnosis of structure;

(b) occurrence of splittings in high resolution spectra

Problems in structure determination

2

Some nuclei with magnetic moments:

^{1}H ^{2}H ^{10}B ^{11}B ^{13}C ^{14}N ^{15}N ^{19}F ^{31}P ^{33}S ^{35}Cl ^{37}Cl

---

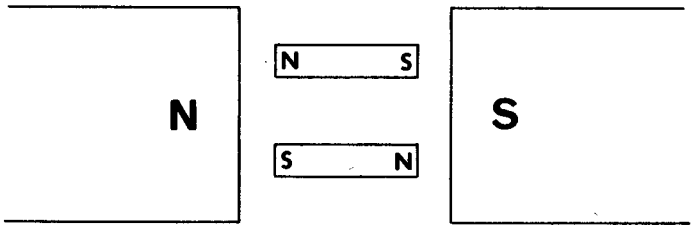
3

Some nuclei with $I = ½$: ^{1}H ^{13}C ^{15}N ^{19}F ^{31}P

Some nuclei with $I = 1$: ^{2}H ^{14}N

Some nuclei with $I = ⅜$: ^{11}B ^{33}S ^{35}Cl ^{37}Cl

4



Orientations of the magnetic moment for a nucleus with $I = ½$, in a magnetic field

5

Number of orientations for a nucleus of spin quantum number I is:

$$2I + 1$$

6

Energies of the two arrangements for a nucleus with $I = ½$:

$$-\mu B \text{ and } +\mu B$$

(μ = magnetic moment; B = magnetic flux density)

7

Condition for absorption of radiation of frequency υ:

$$h\upsilon = 2\mu B$$

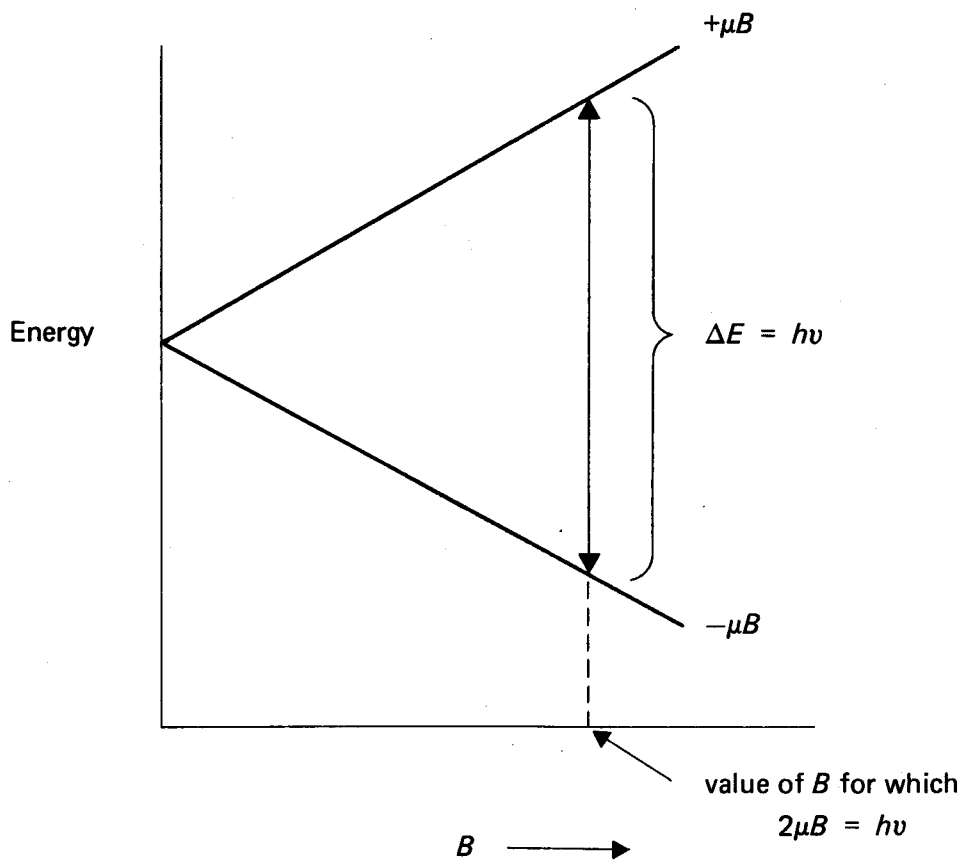
For ^{1}H: if $B = 1.41$ T (Tesla) (14,100 Gauss),

$$\upsilon = 60 \text{ MHz}$$

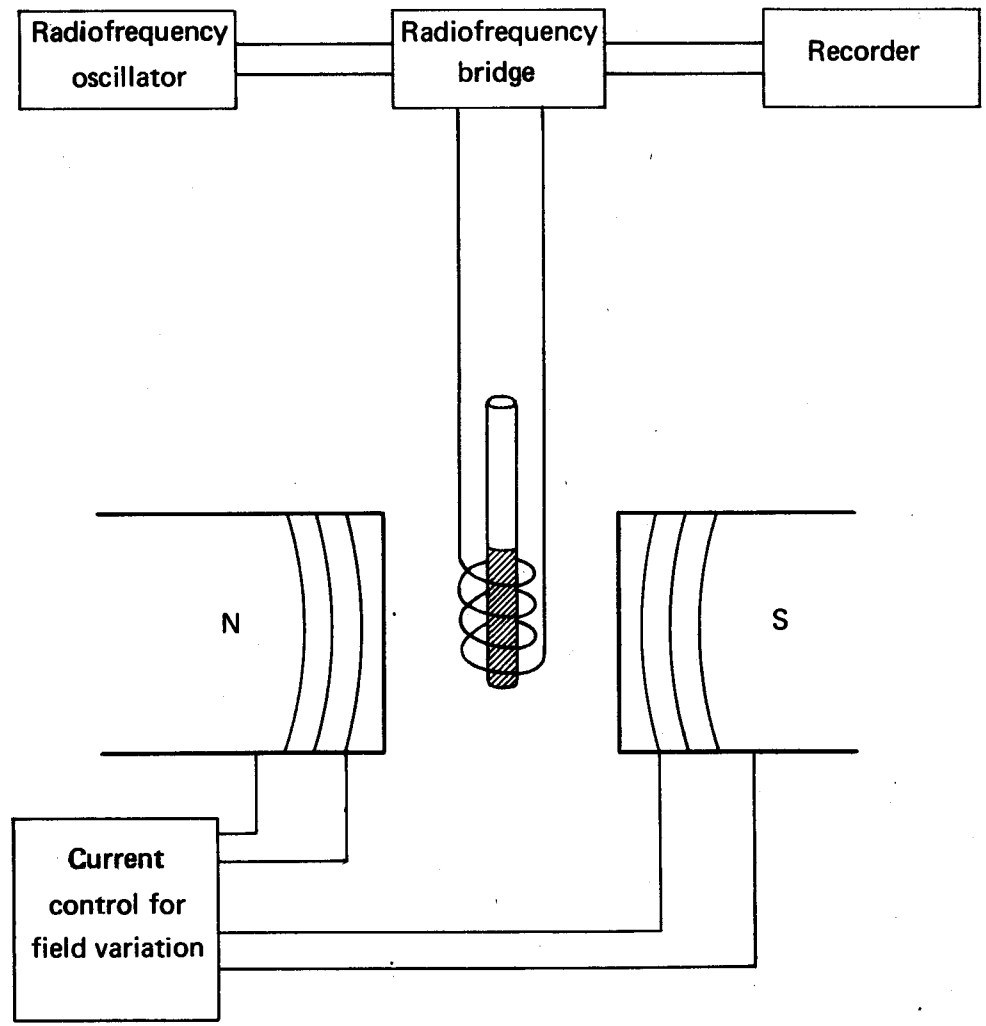
8

Calculate the field, B, necessary for proton (^{1}H) n.m.r. for a frequency of 100 MHz

Effect on the energies of the two spin states of increasing the applied magnetic field



Basic features of a continuous wave spectrometer



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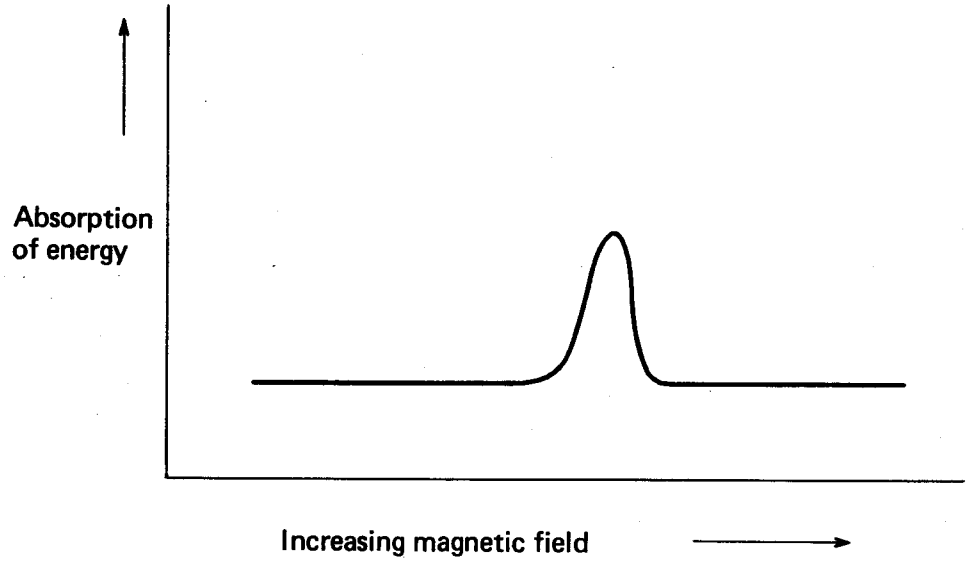


12

Distribution of nuclei of magnetic moment μ between upper and lower energy levels in a magnetic field B:

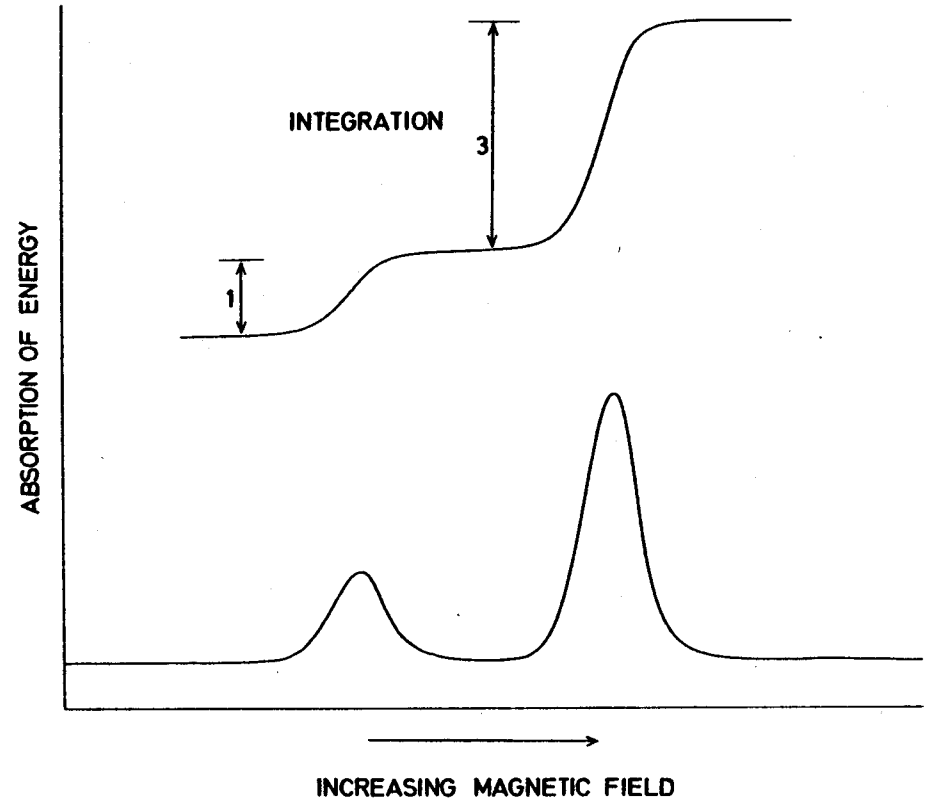
$$N_U/N_l = e^{-\Delta E/kT} = e^{-2\mu B/kT}$$

13

$$h\upsilon = 2\mu B$$

For ^{13}C: if υ = 20 MHz, B = 1.86 T

14



Low resolution ^1H n.m.r. spectrum of methanol, CH_3OH

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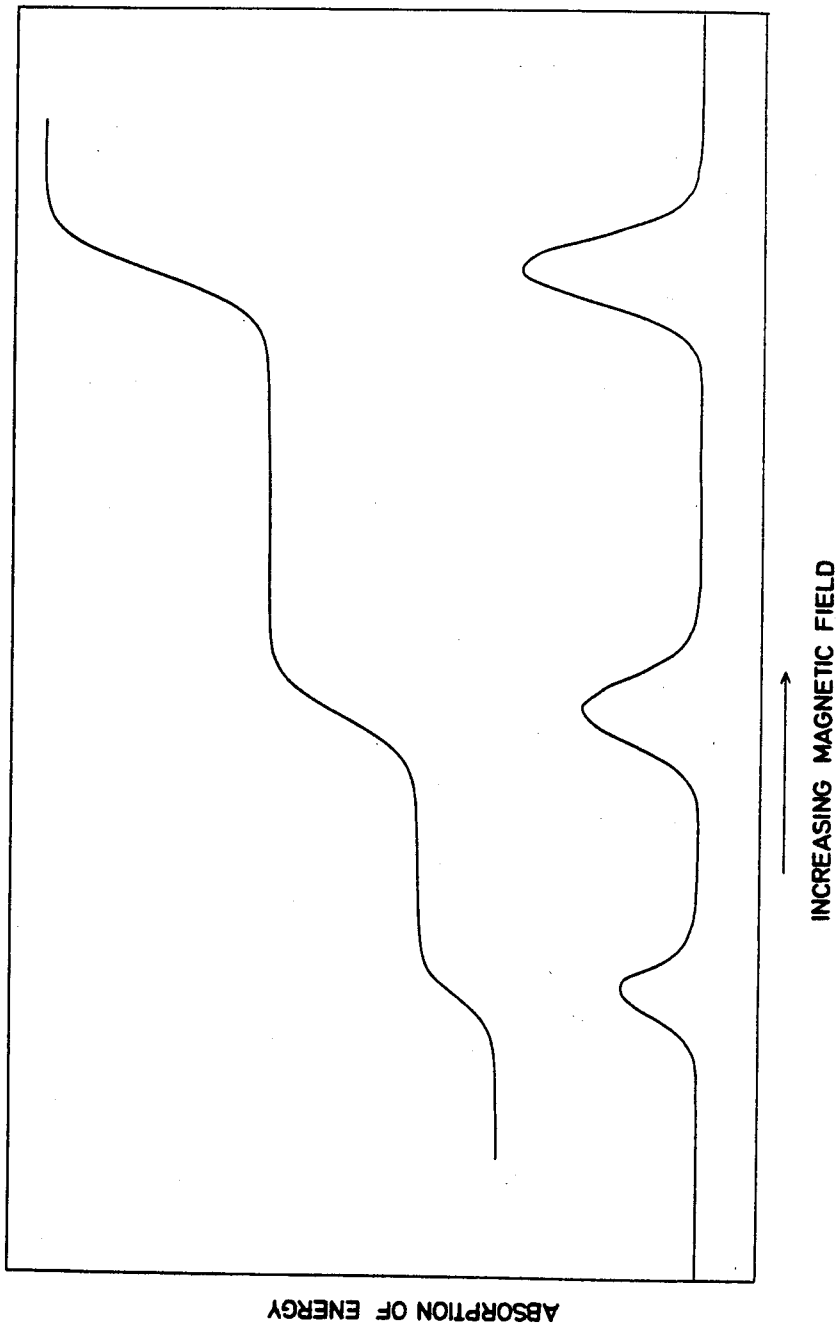
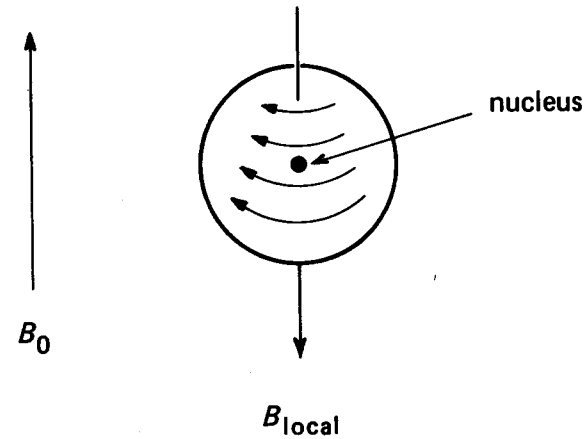


Low resolution ^1H n.m.r. spectrum for analysis

16

The origin of a local magnetic field, B_{local}: this is produced by circulation of the electron cloud around the nucleus induced by the applied field B_0.



17

The chemical shift scale, δ, related to $Si(CH_3)_4$ (TMS):

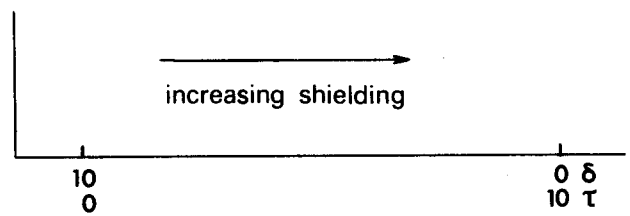
$$\delta = \frac{\Delta B}{B} \times 10^6$$

where $\Delta B = B_{standard} - B_{sample}$, for constant frequency

$$\delta = \frac{\Delta \upsilon}{\upsilon} \times 10^6 \quad \text{for constant magnetic field}$$

18

$$\tau = 10 - \delta$$



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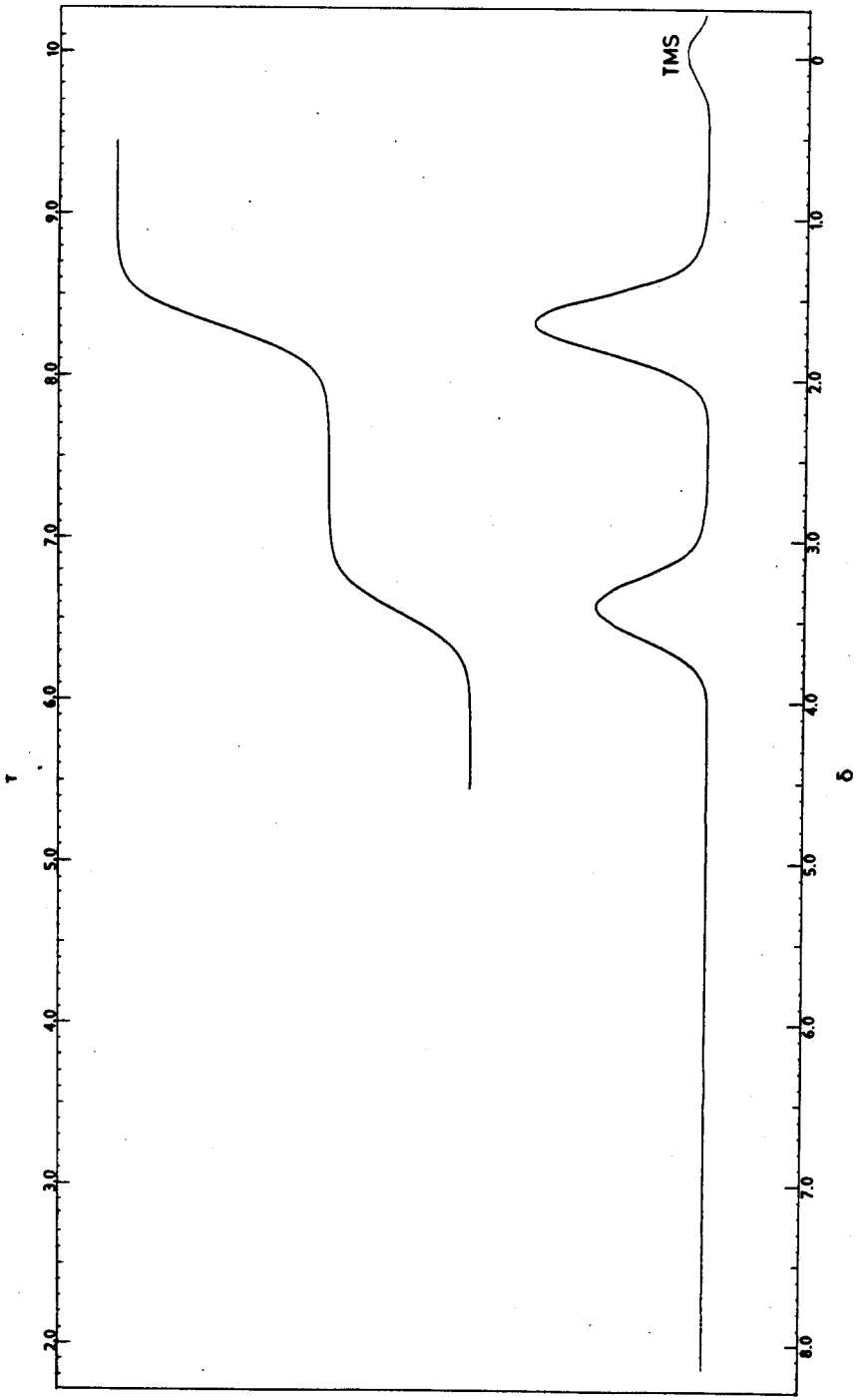

Low resolution ^1H n.m.r. spectrum of bromoethane, CH_3CH_2Br, with TMS added

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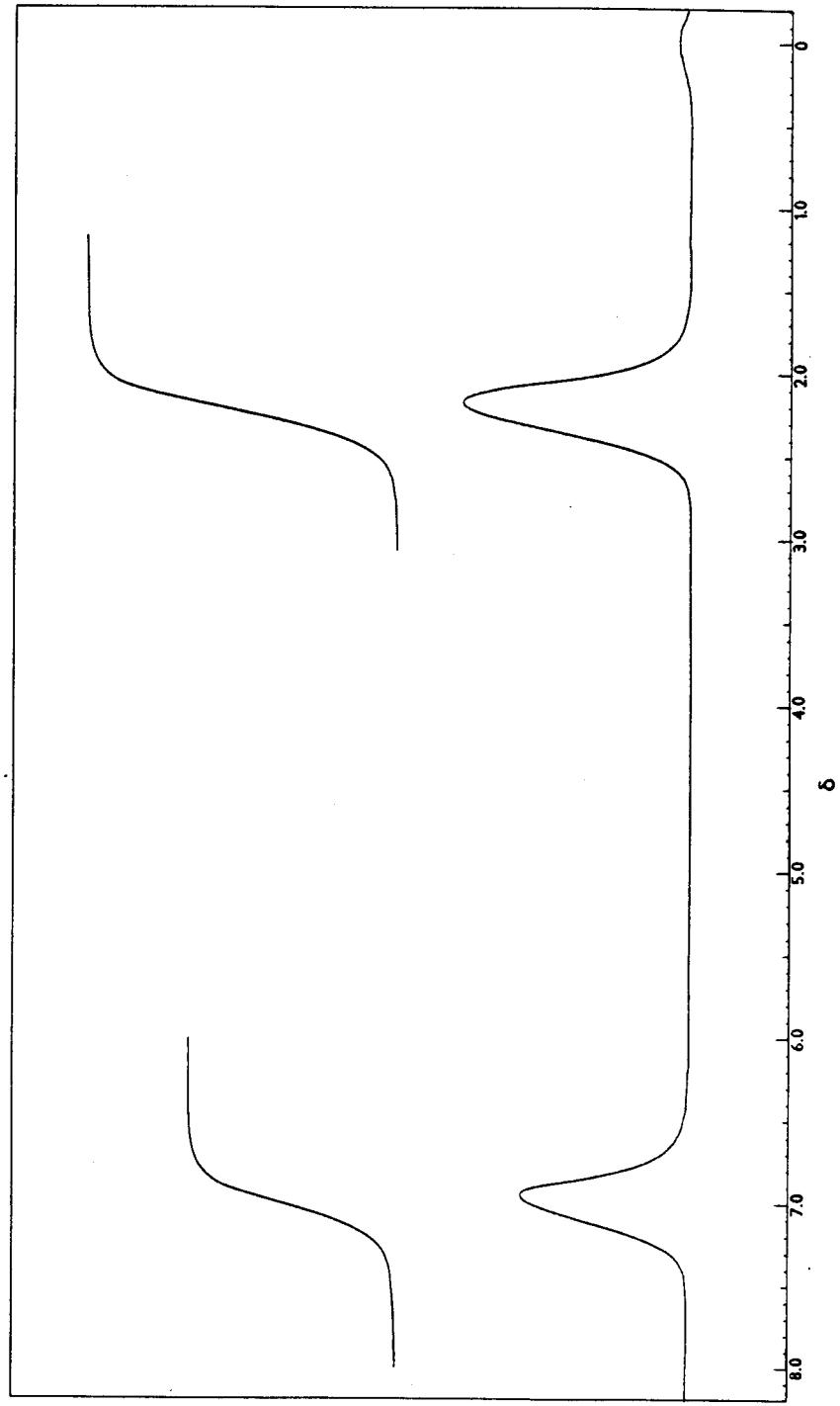
Some values of the chemical shift, δ

CH_3-CH_2-OH		CH_3-CH_2-Br	
1.15	3.6	1.65	3.4

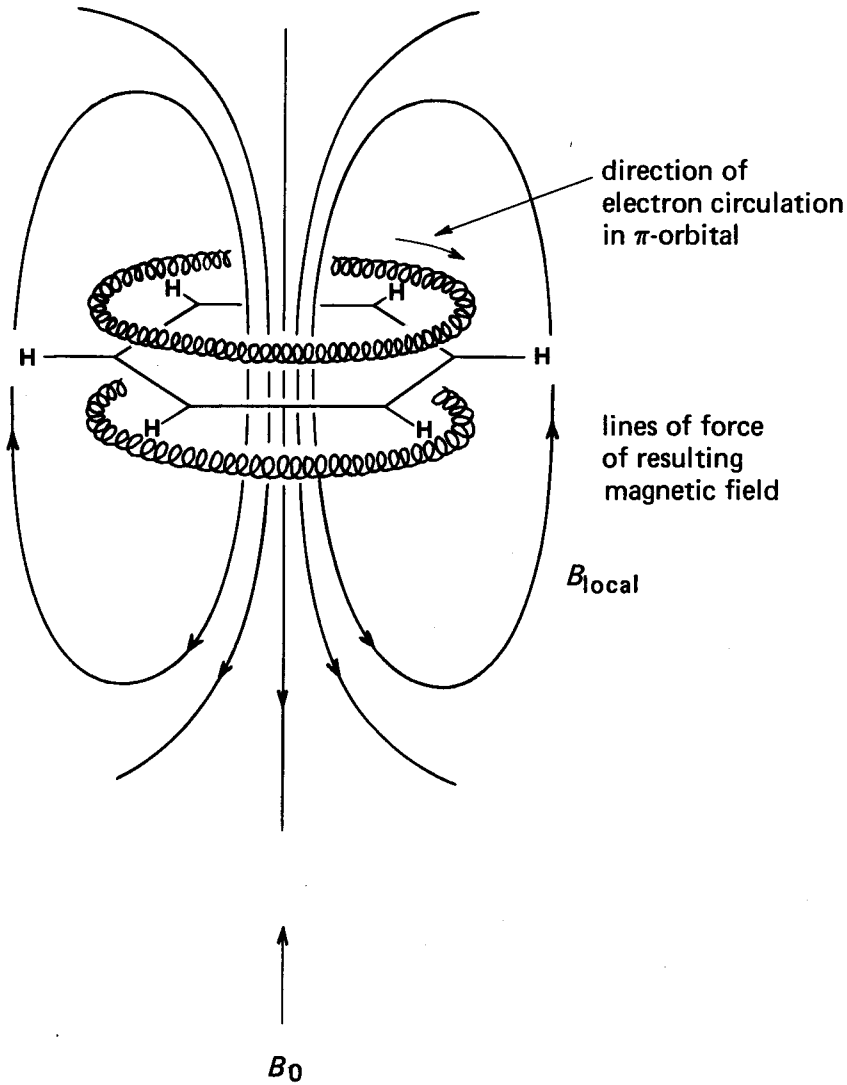
21

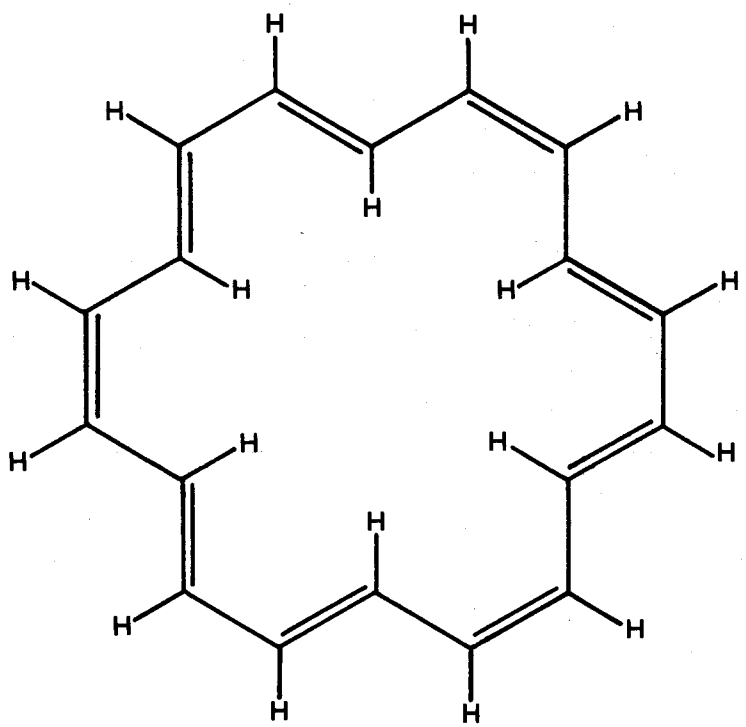


^{1}H n.m.r. spectrum of 1,4-dimethylbenzene

22

Induced electron circulation in benzene: the production of a local magnetic field at the proton which augments the applied field





[18] –Annulene

12H δ 9.3 ppm
6H δ -3.0 ppm

Table of typical values of chemical shifts for protons in organic molecules

Group	Compound type	Chemical shift/δ
CH_3–C	alkane	0.9
CH_3–C(=O)–	ketone	2.1
CH_3–O–	ether	3.3
H–C=C–	alkene	4.5–8
H–C_6H_5	arene	6–9
H–C(=O)–	alkanal	9.7

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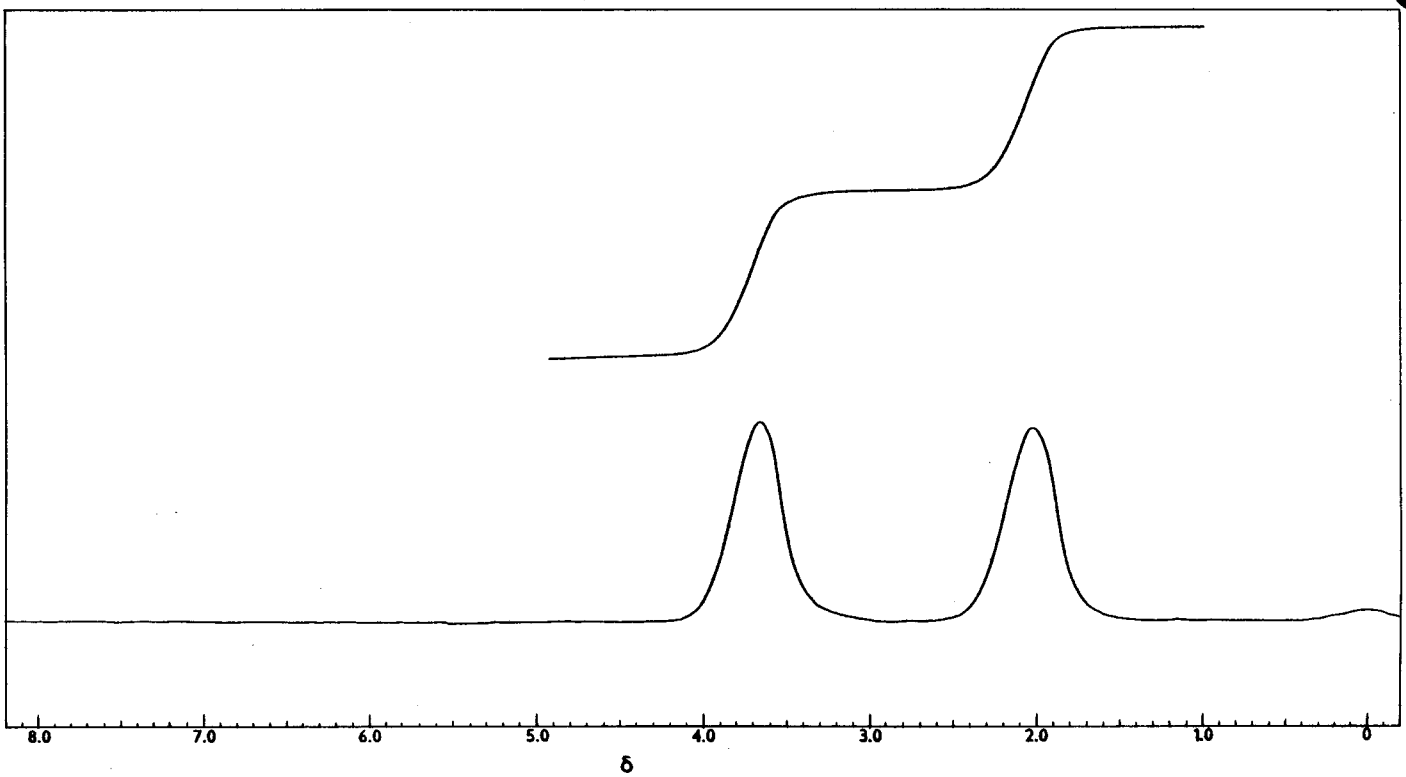
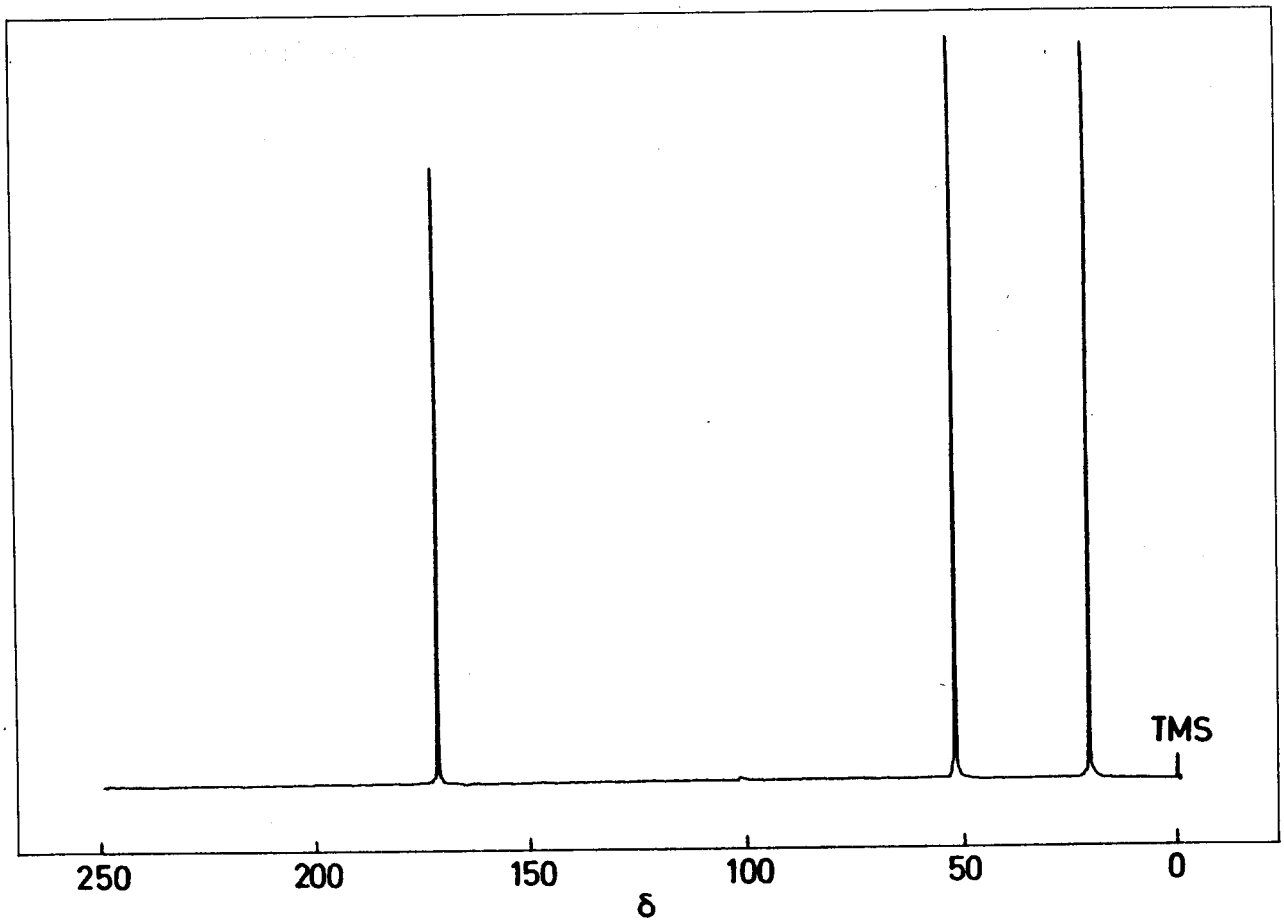


^{1}H n.m.r. spectrum of a compound $C_3H_6O_2$



^{13}C n.m.r. spectrum of methyl ethanoate, $CH_3C(=O)OCH_3$

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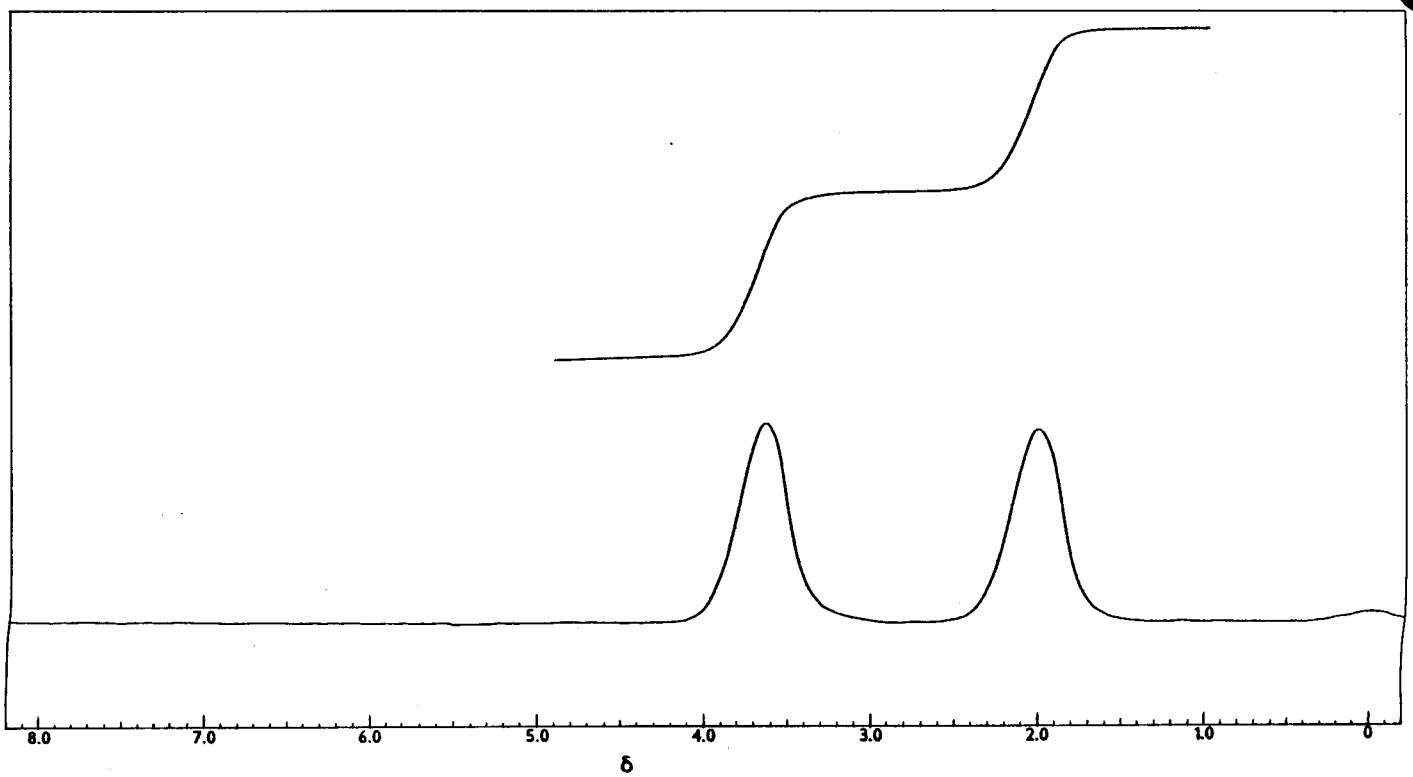
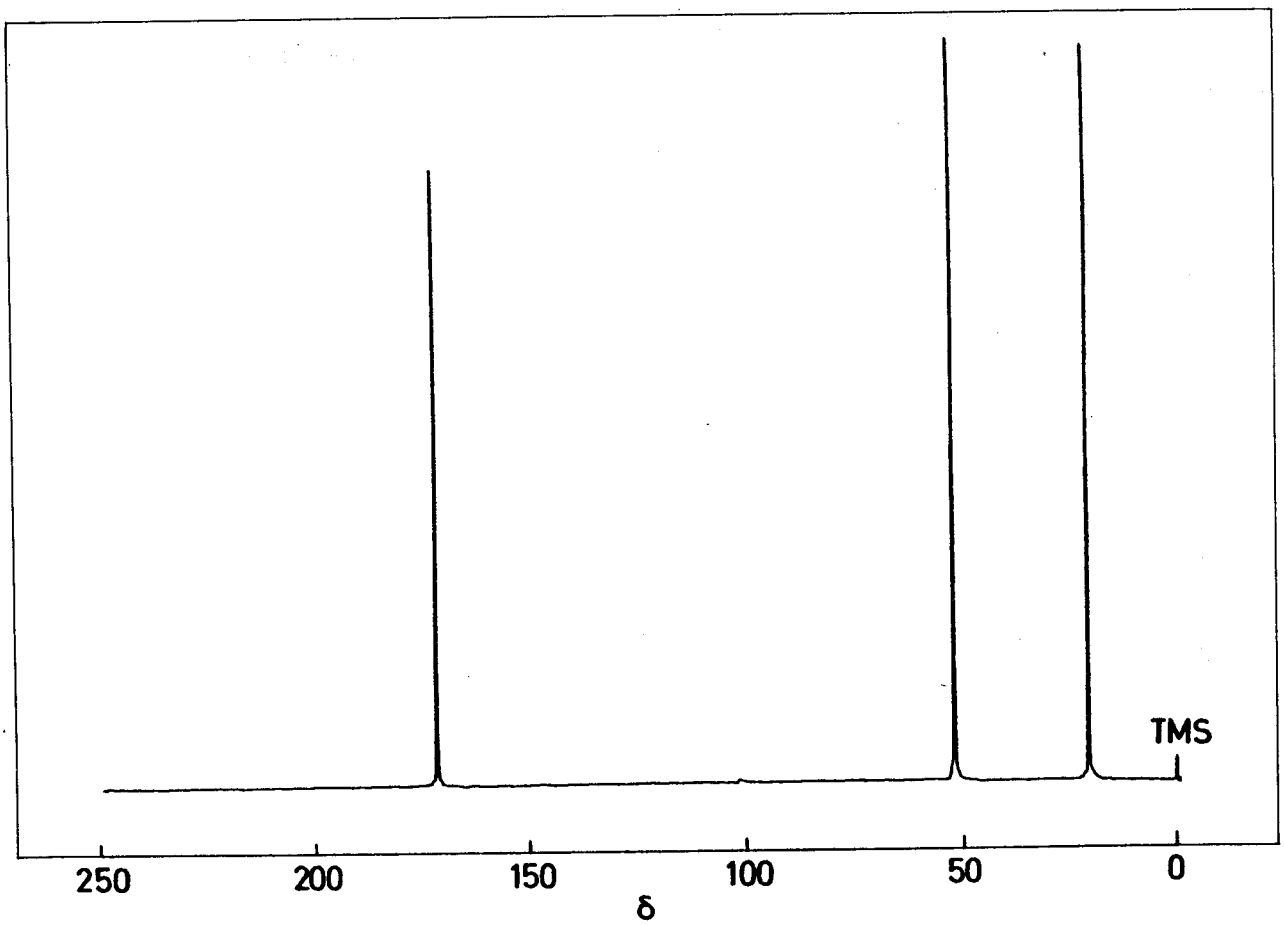


^{1}H n.m.r. spectrum of a compound $C_3H_6O_2$

26



^{13}C n.m.r. spectrum of methyl ethanoate, $CH_3C(=O)OCH_3$

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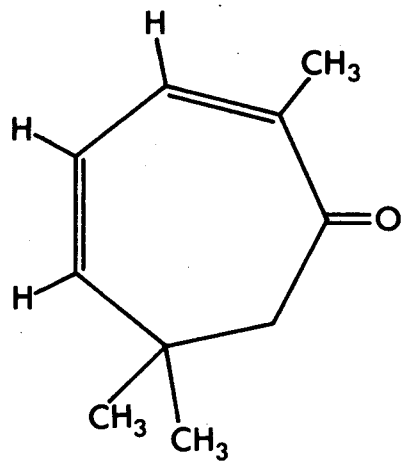
Proposed structures for Eucarvone



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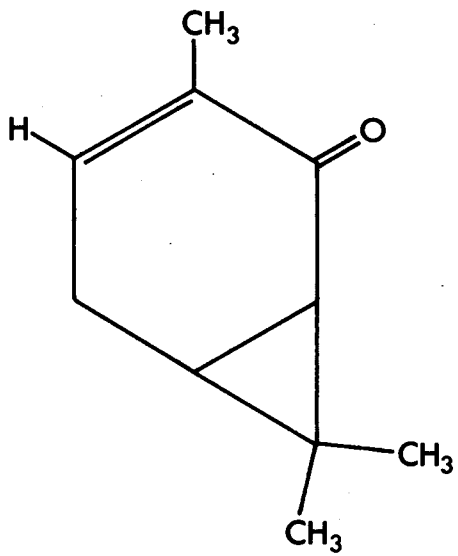

B

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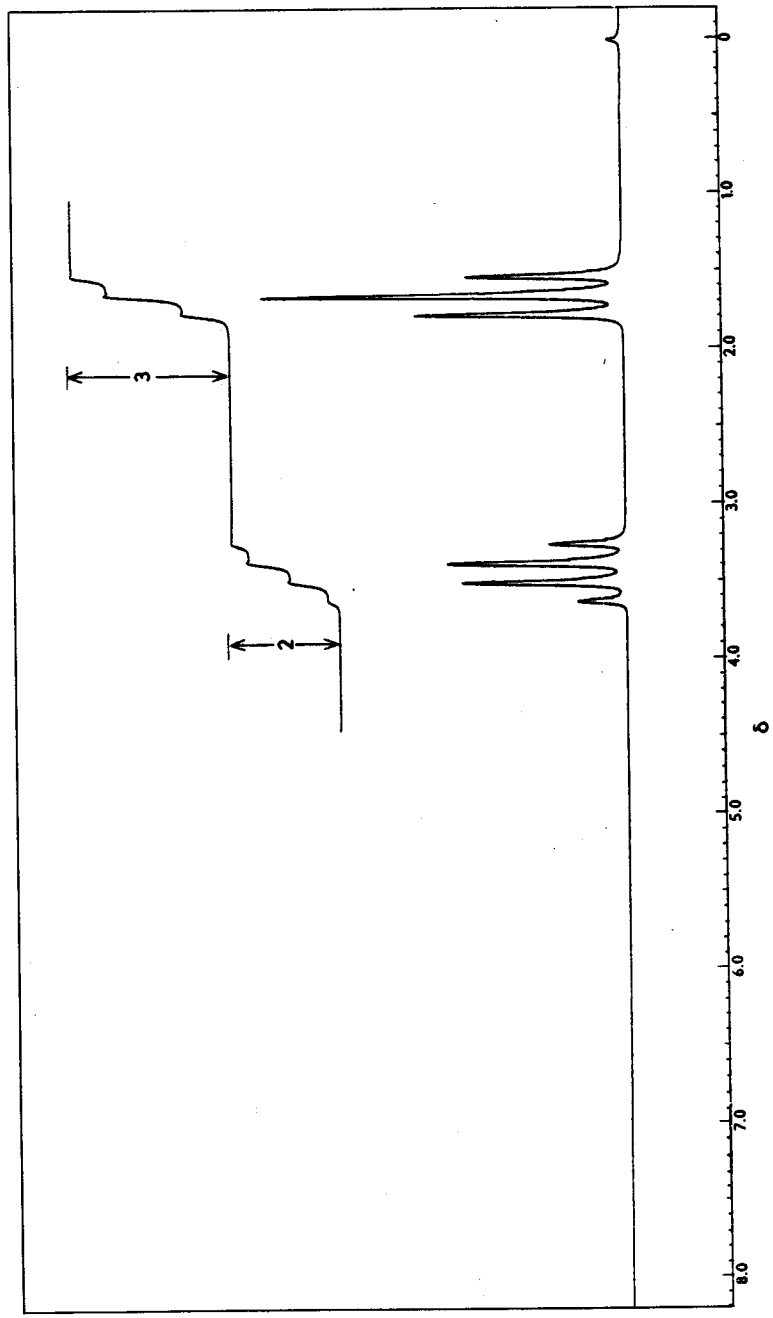
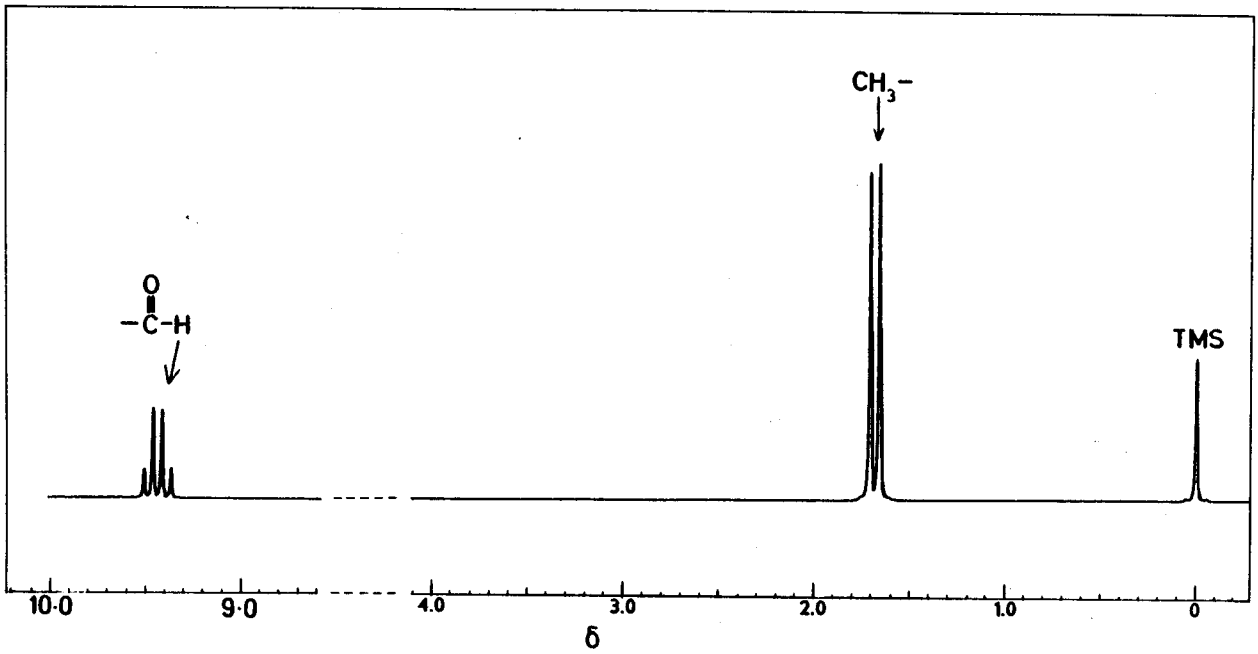
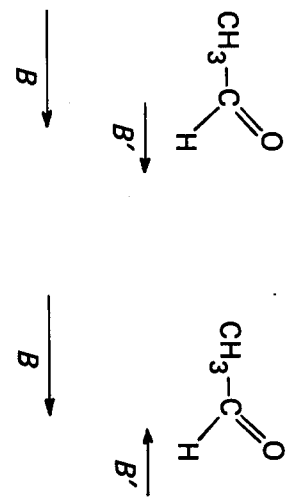


High resolution ^1H n.m.r. spectrum of bromoethane, CH_3CH_2Br



High resolution ^{1}H n.m.r. spectrum of ethanal, CH_3CHO



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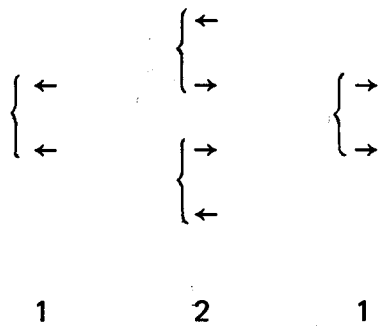
Arrangements of the magnetic moments of the protons in the CH_2 group:



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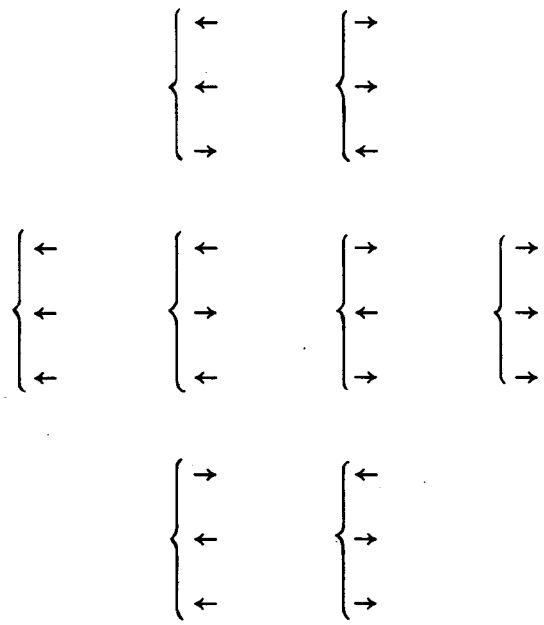

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Number of protons causing splitting	Splitting pattern (relative intensities)
1	1 1
2	1 2 1
3	1 3 3 1
4	1 4 6 4 1
5	1 5 10 10 5 1
6	1 6 15 20 15 6 1

34

Information from n.m.r. spectra

Features	**Information obtained about:**
Integration trace	*Number* of protons in each group of different type
Chemical shifts	The chemical environment or *type* of each group of protons
Splittings	*Number* of protons on atoms adjacent to the group which contains the proton(s) whose resonance is being recorded

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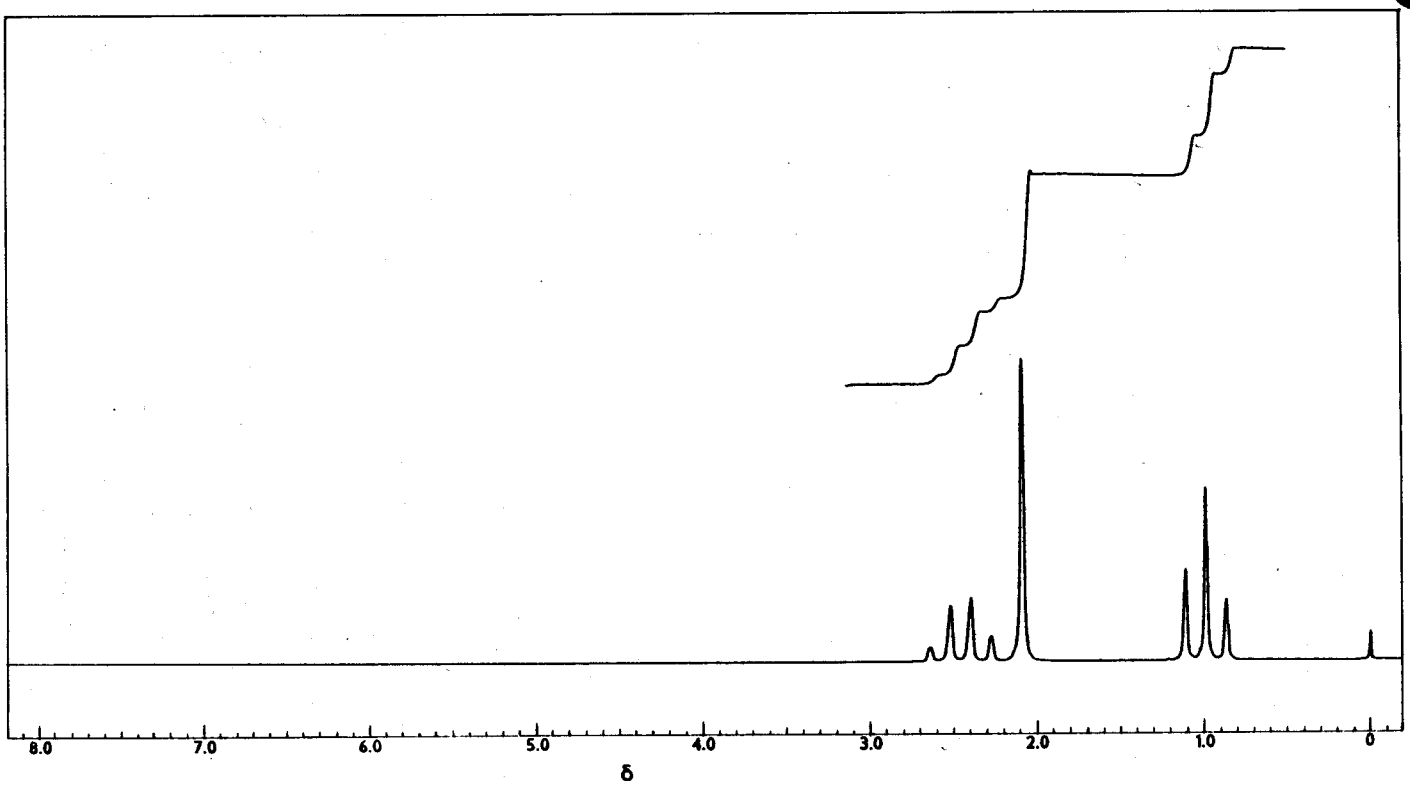

^{1}H n.m.r. spectrum of a compound C_4H_8O

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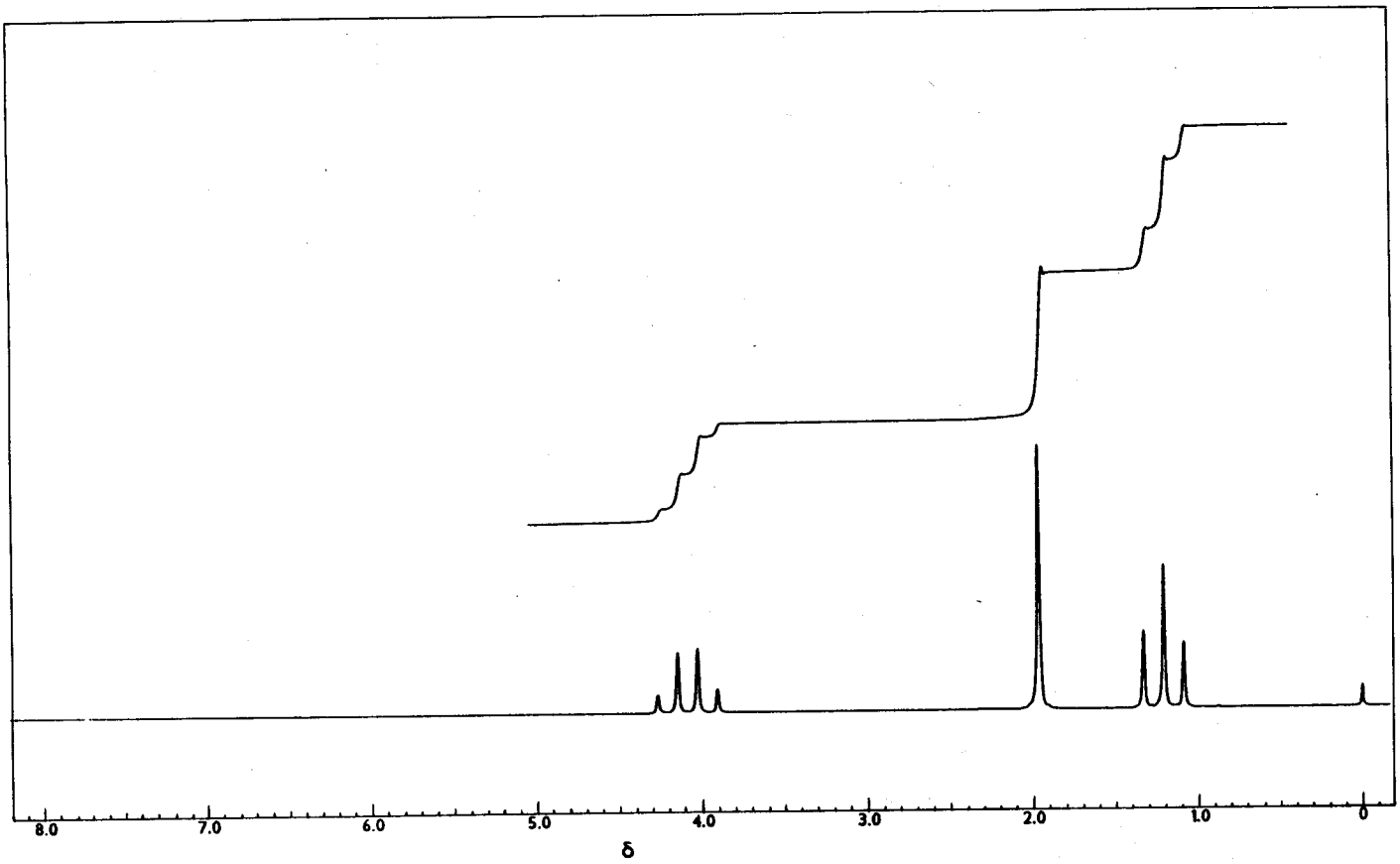

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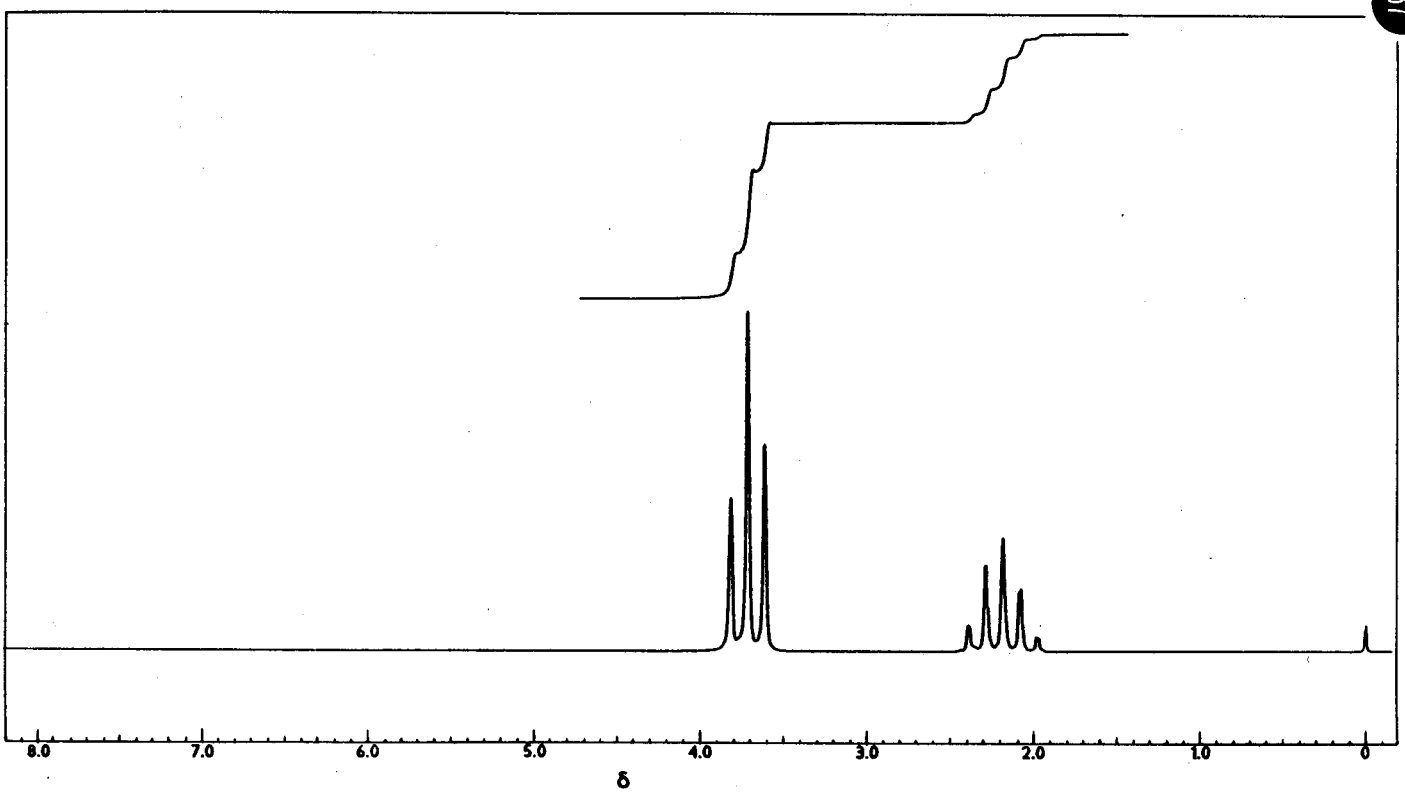

^{1}H n.m.r. spectrum of a compound $C_3H_6Cl_2$

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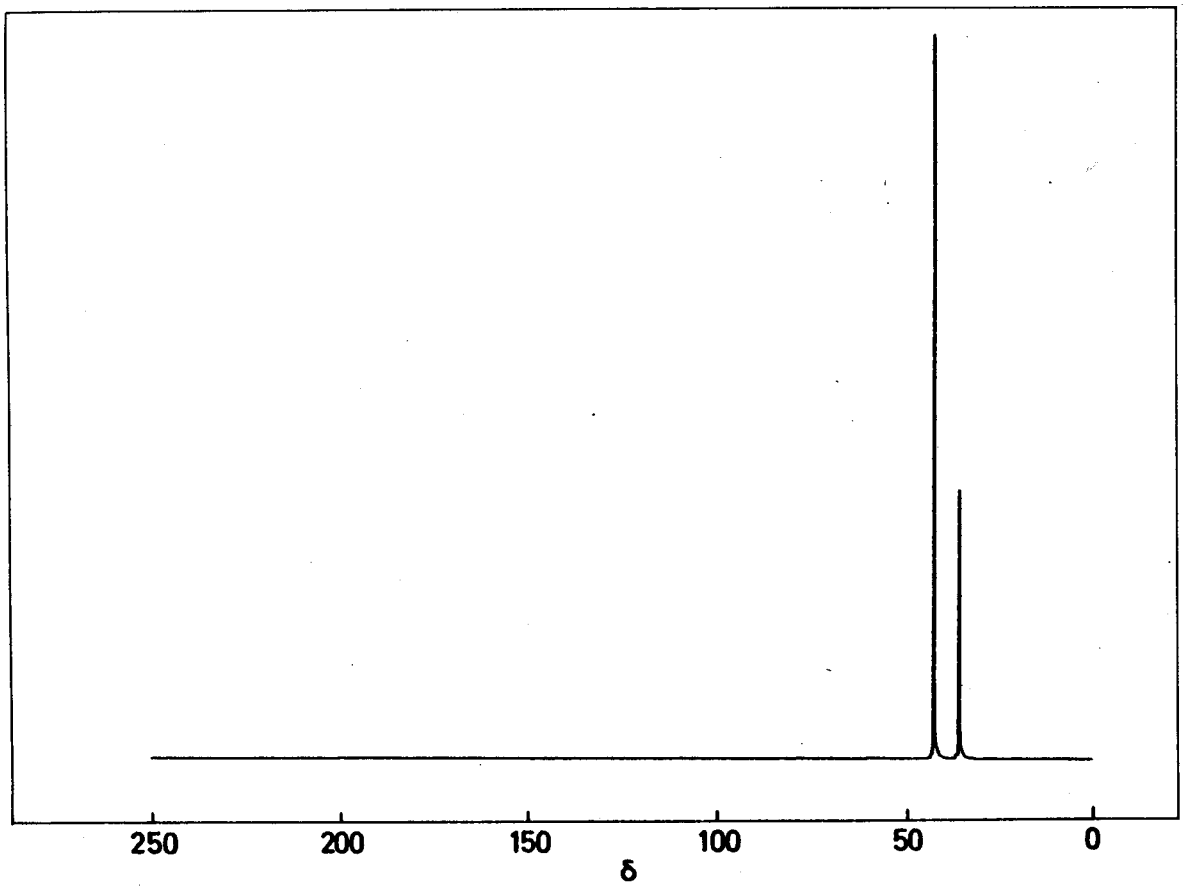
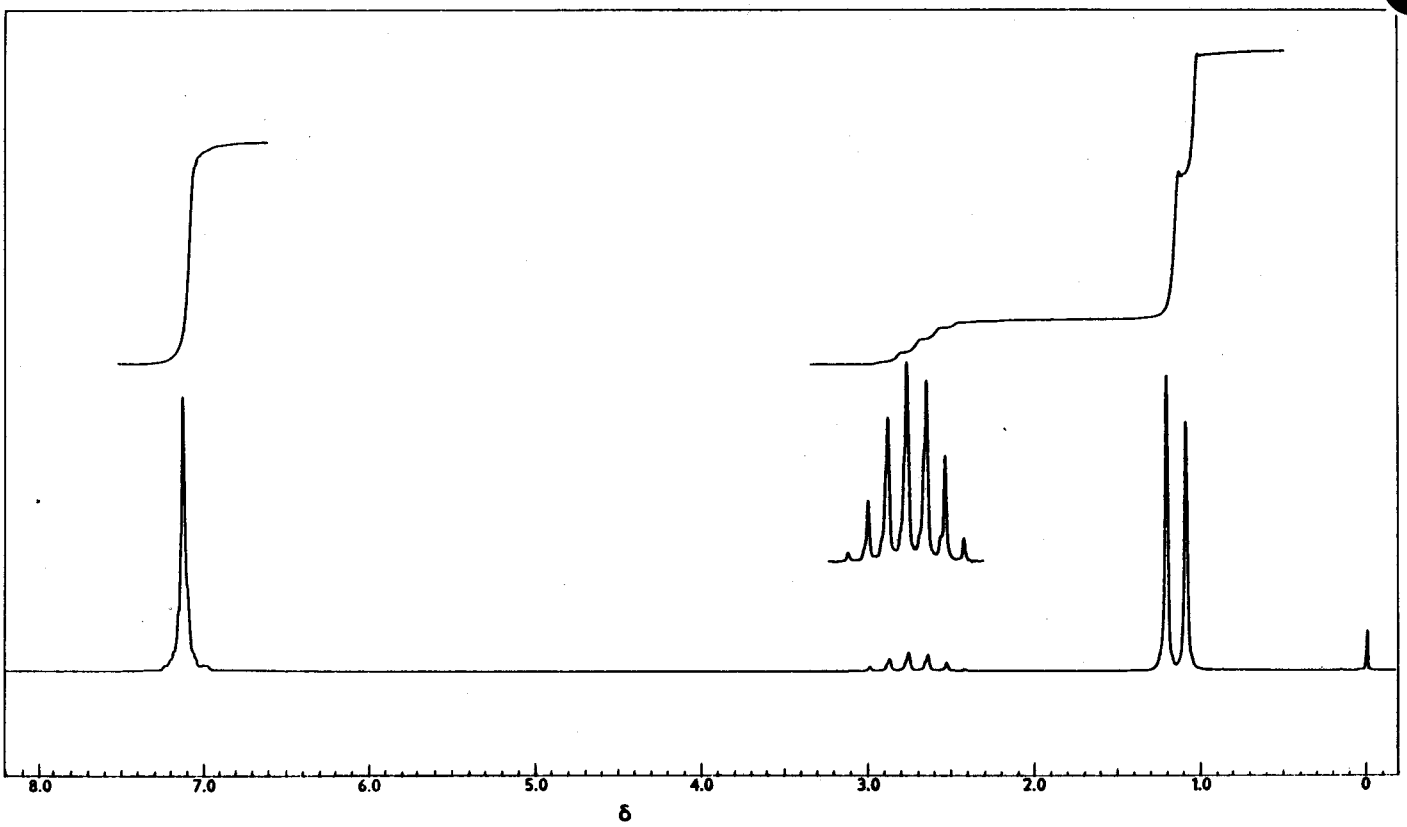
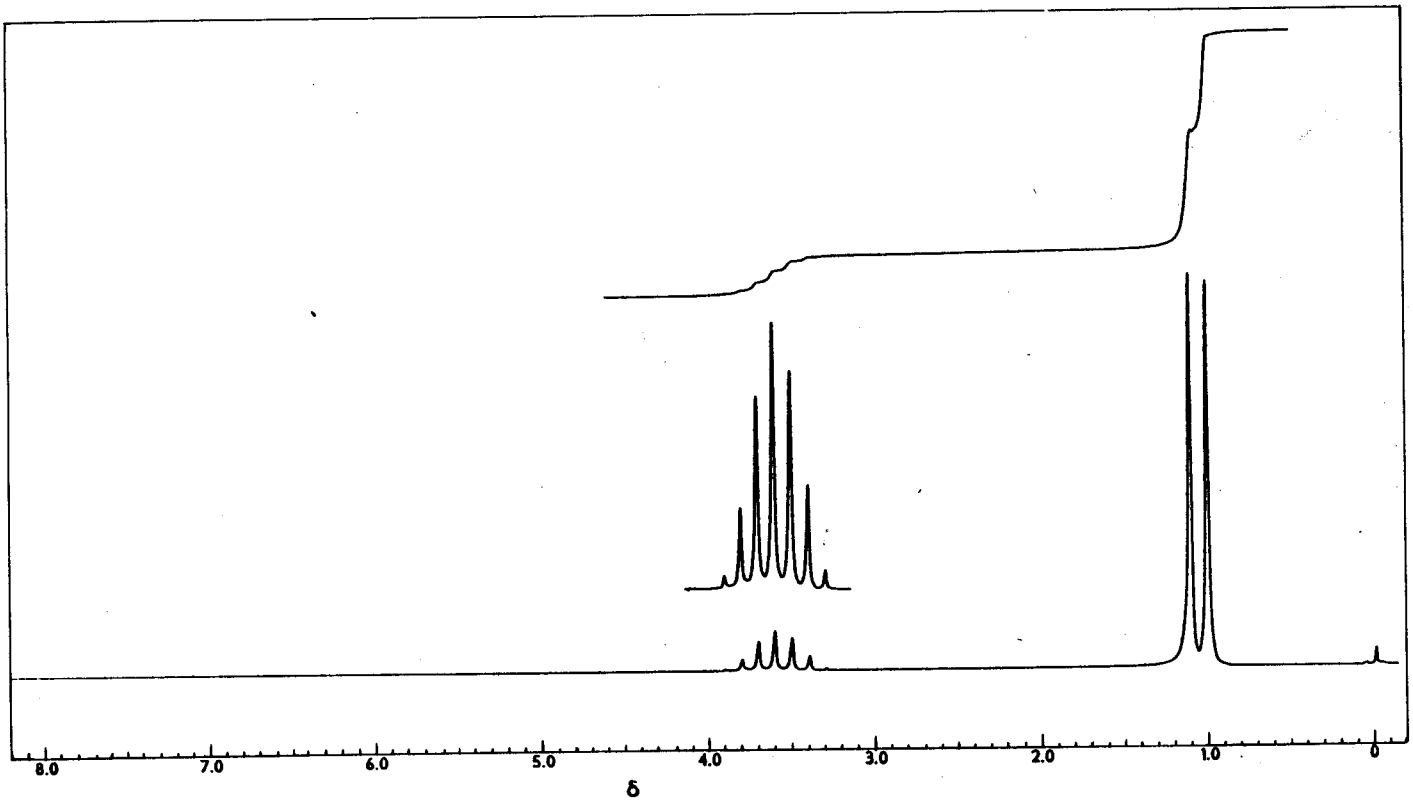


^{13}C n.m.r. spectrum of $ClCH_2CH_2CH_2Cl$

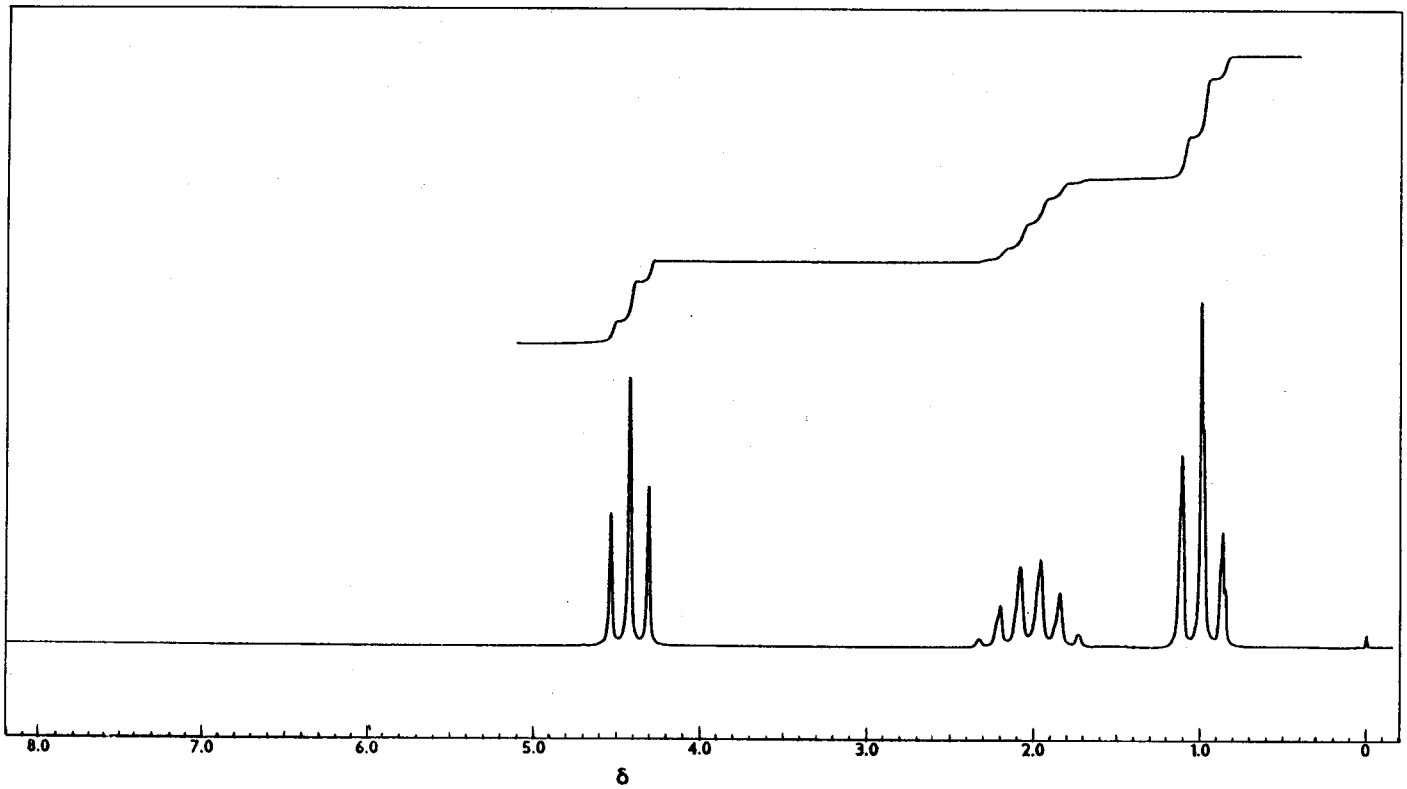


^1H n.m.r. spectrum of a compound C_9H_{12}; the absorption centred at δ 2.75 is also shown enlarged.

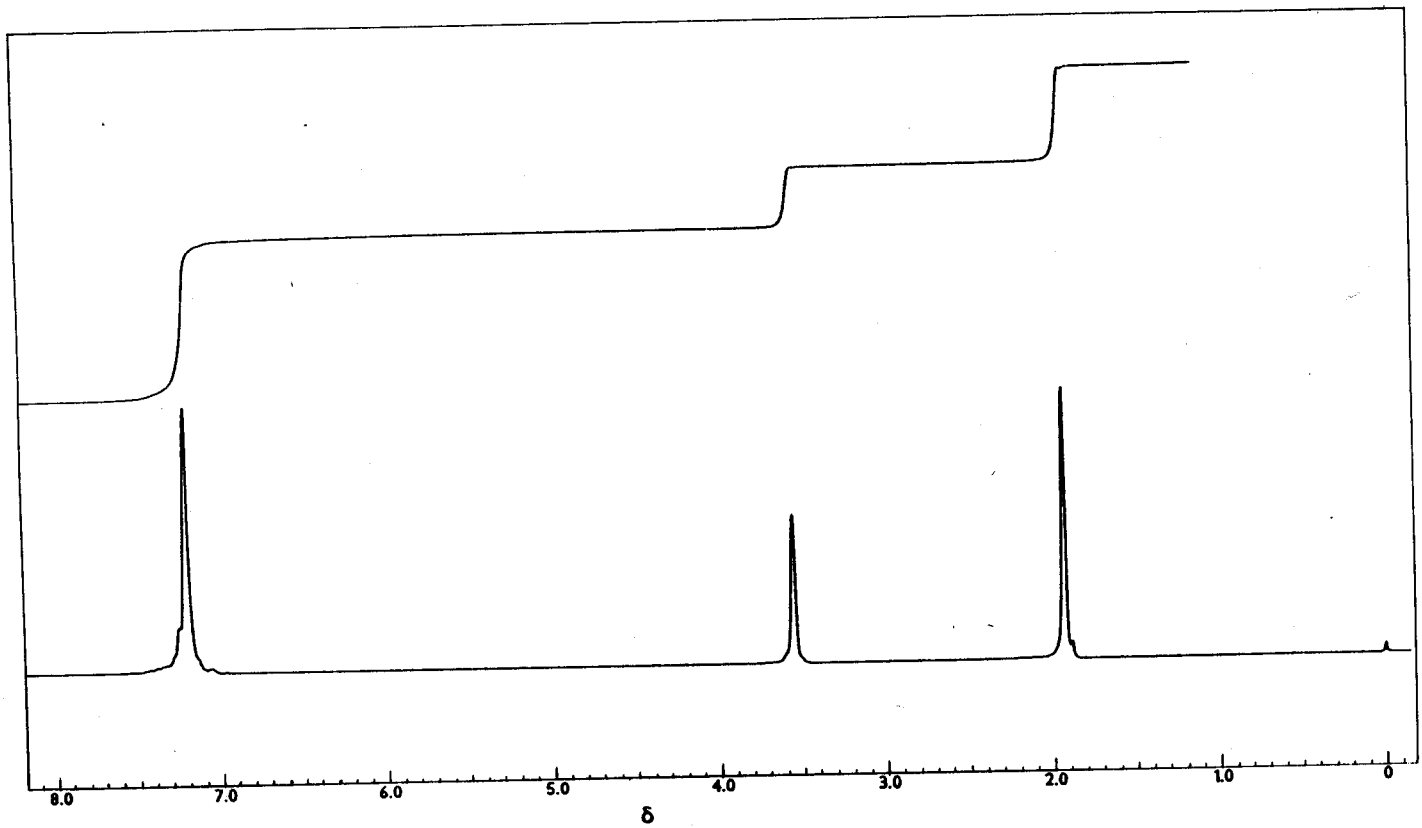


1. ^1H n.m.r. spectrum of a compound $C_6H_{14}O$

Problems for the end of Side 1



2. ^1H n.m.r. spectrum of a compound $C_3H_7NO_2$



3. ^1H n.m.r. spectrum of a compound $C_9H_{10}O$

Topics described on the second side

Splittings: their measurement and their dependence on structure

Second-order effects, and nomenclature used in describing spectra

Modification of the appearance of spectra:

(a) spectra at 60 and 100 MHz

(b) use of shift reagents

(c) decoupling

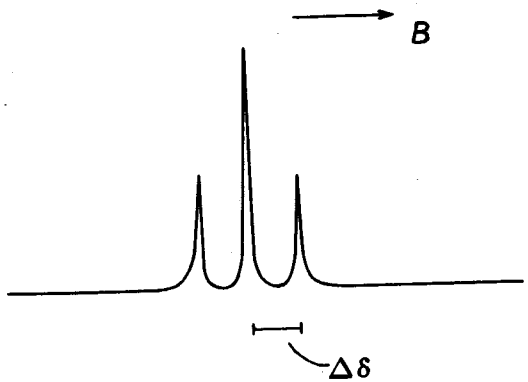
Dynamic processes studied by n.m.r.: proton-exchange, internal rotation, conformational interconversion

Tautomerism

^{13}C n.m.r.: methods of recording spectra, and examples of use

Applications of n.m.r. to inorganic examples

A typical 1:2:1 splitting pattern:



Separation between peaks = $\Delta\delta$

Splitting J = $\Delta\upsilon$ in frequency units (Hz)

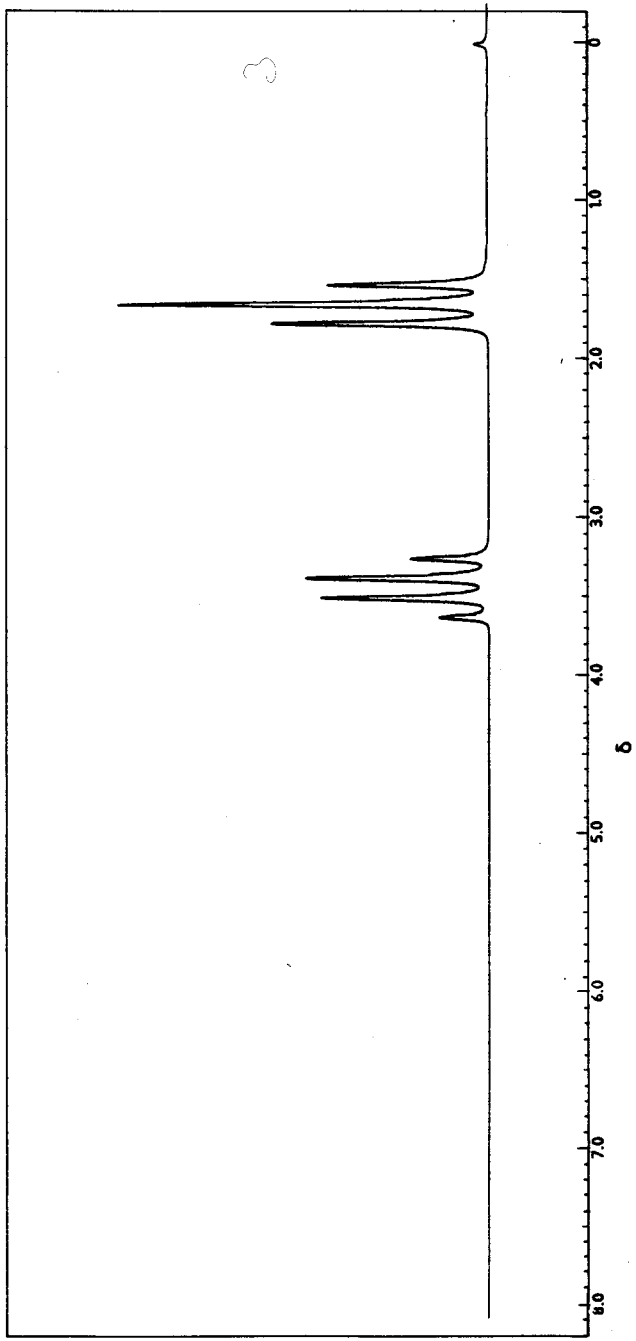
Since $\Delta\delta = \frac{\Delta B}{B} \times 10^6$

(from the definition of the δ scale)

and $\frac{\Delta\upsilon}{\upsilon} = \frac{\Delta B}{B}$

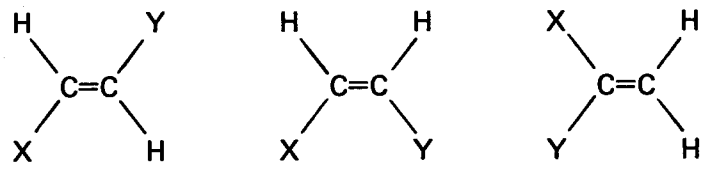
(from the relationship $h\upsilon = 2\mu B$, where υ is the frequency of the spectrometer)

$$\therefore \boxed{J = \Delta\upsilon = \frac{\Delta\delta \times \upsilon}{10^6}}$$



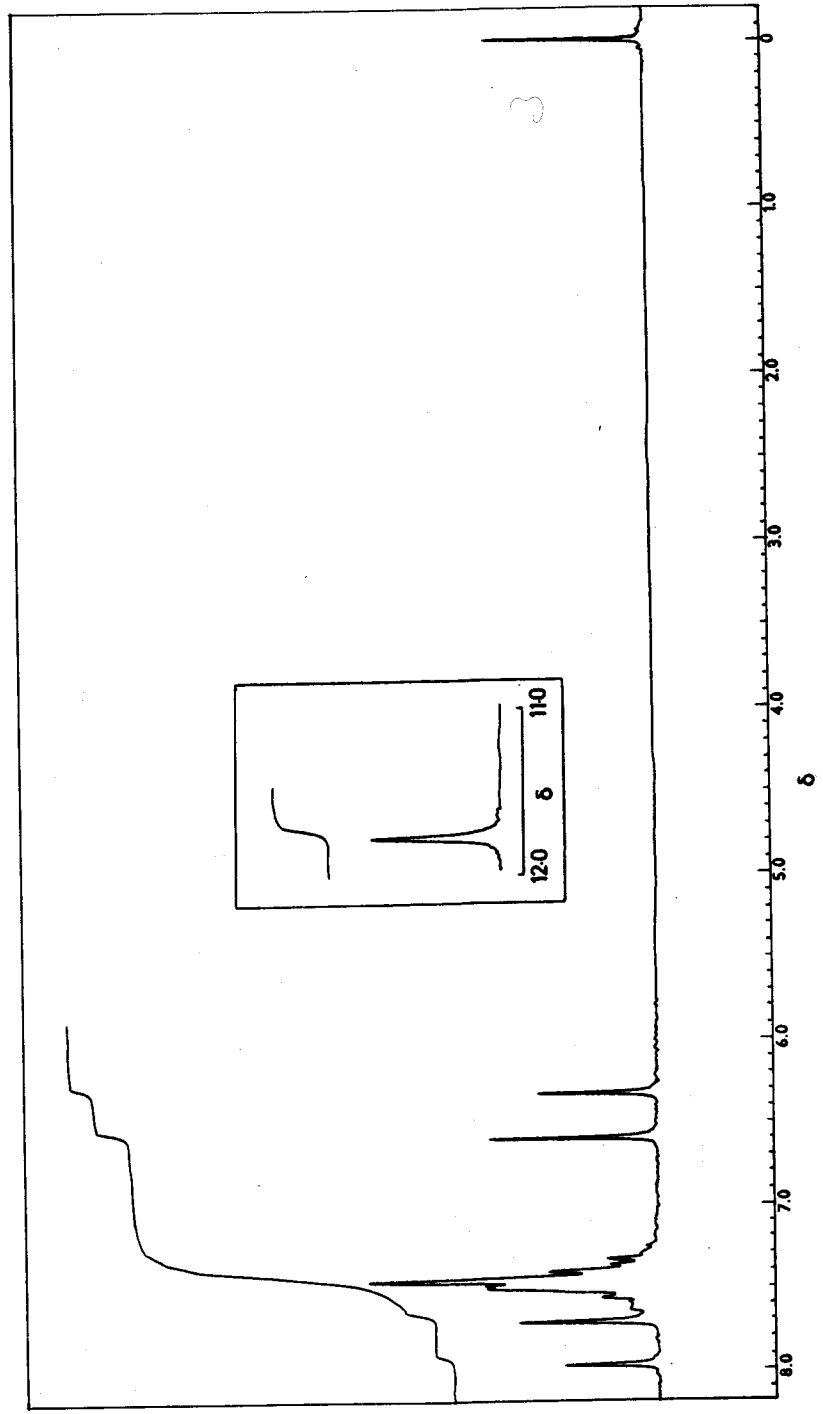
^{1}H n.m.r. spectrum of bromoethane, CH_3CH_2Br (recorded on a spectrometer with υ 60 MHz)

43

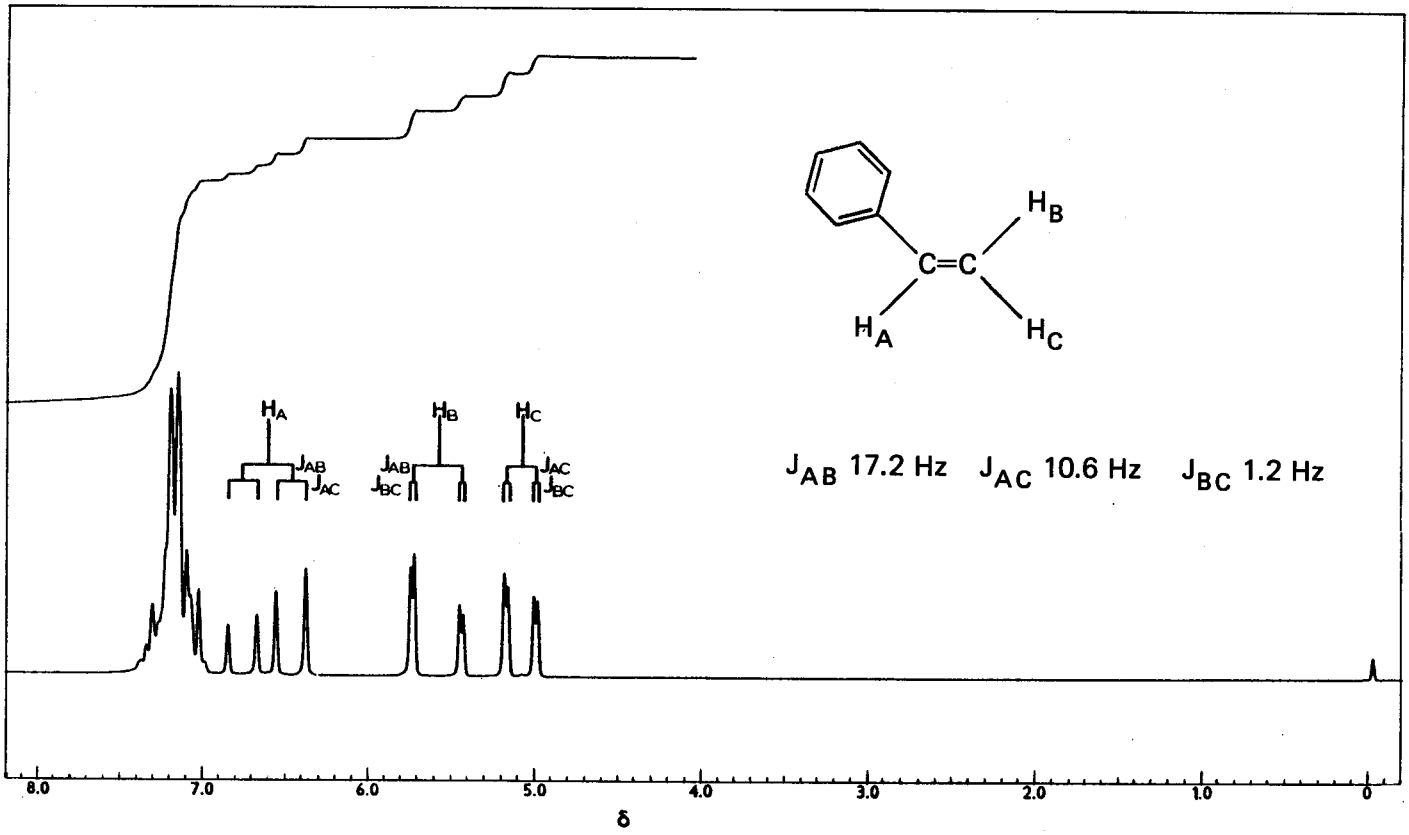


J_{HH} 12-18 Hz 6-12 Hz 0-3 Hz

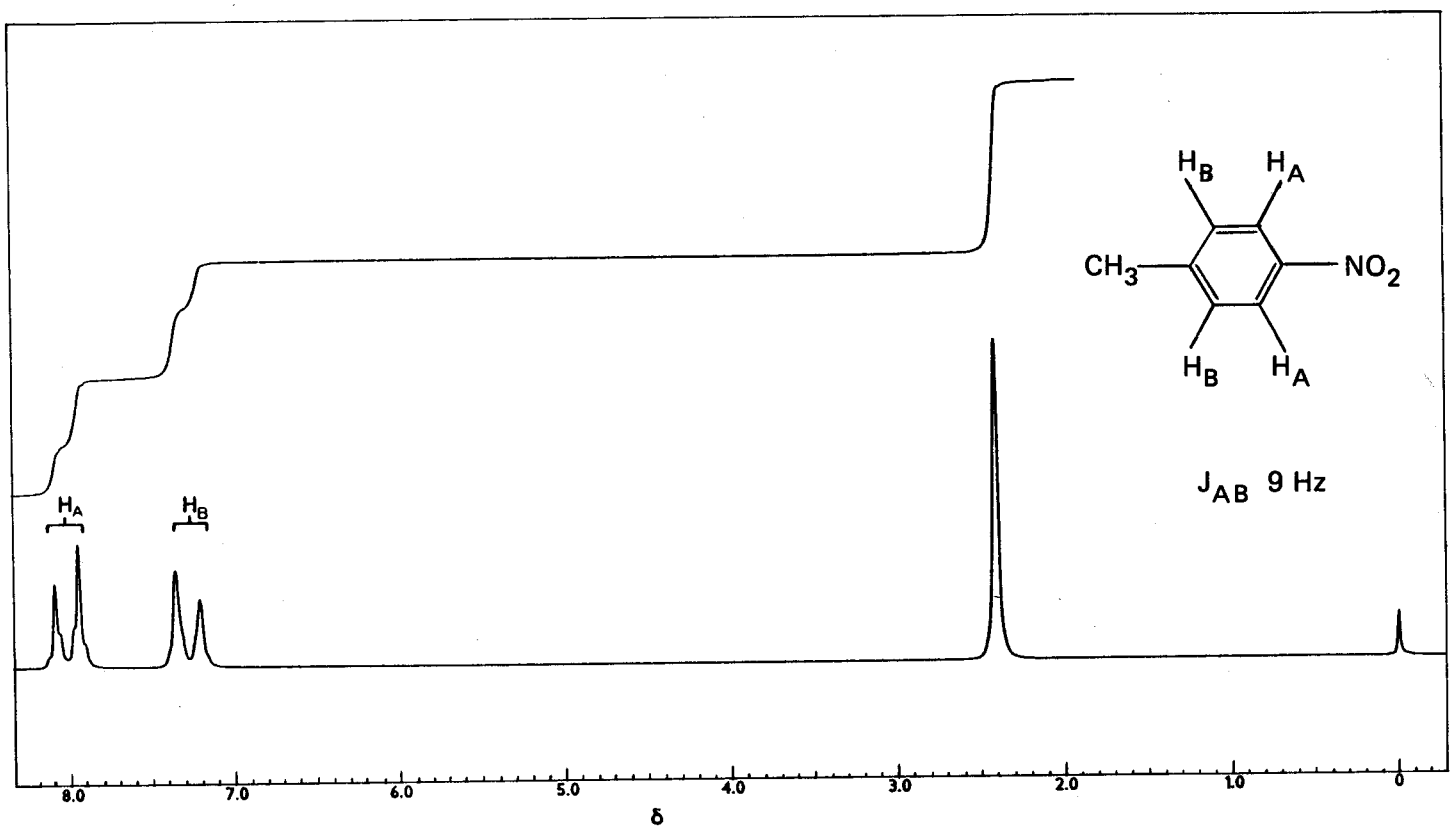
44



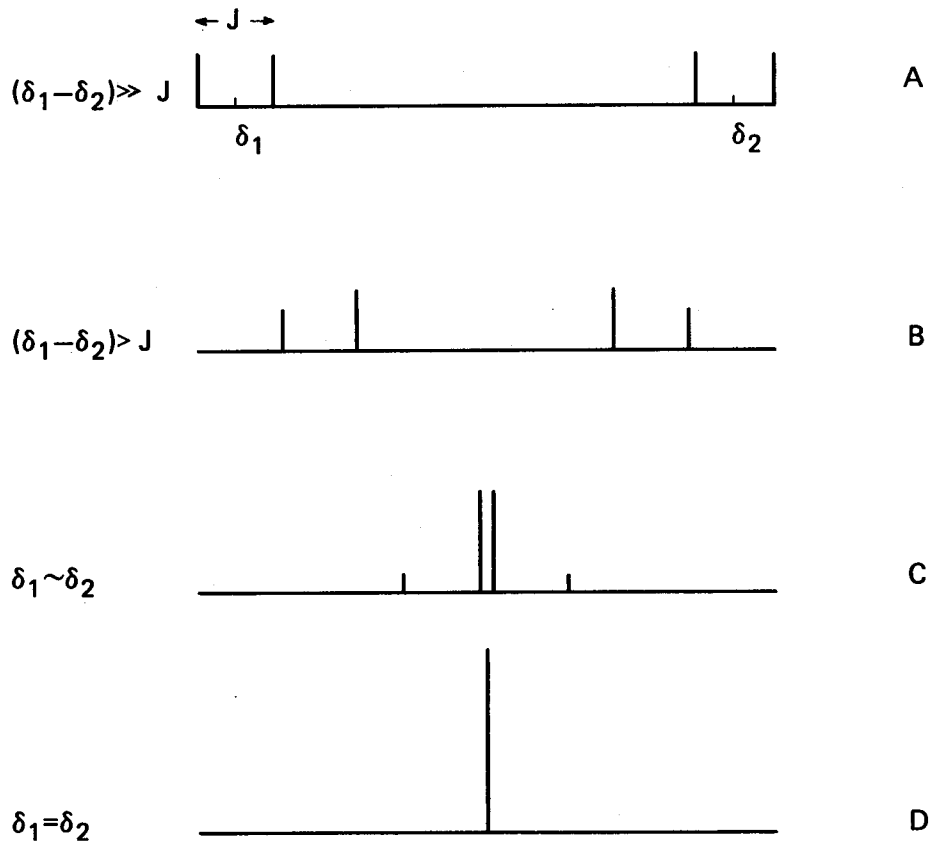
^{1}H n.m.r. spectrum of 3-phenylpropenoic acid, $C_6H_5CH{=}CHCO_2H$ (recorded at 60 MHz); J_{HH} = 16 Hz



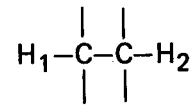
^{1}H n.m.r. spectrum of phenylethene, $C_6H_5CH{=}CH_2$ (recorded at 60 MHz)



^{1}H n.m.r. spectrum of methyl-4-nitrobenzene, 4-$CH_3C_6H_4NO_2$ (recorded at 60 MHz)



Description of the spectra of molecules with two non-equivalent protons, H_1 and H_2

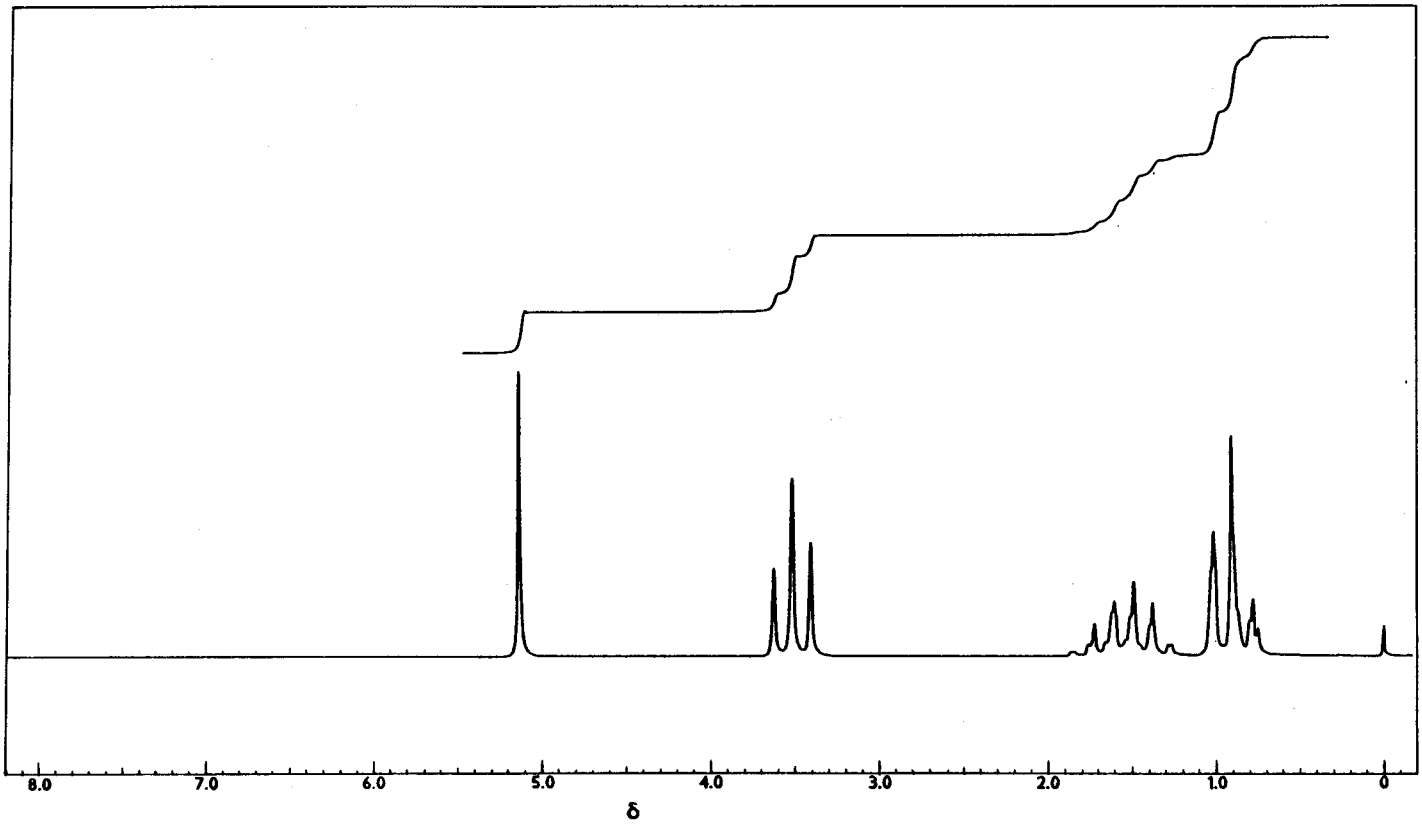


For $\delta_1-\delta_2 \gg J$, spectrum is referred to as 'AX' type

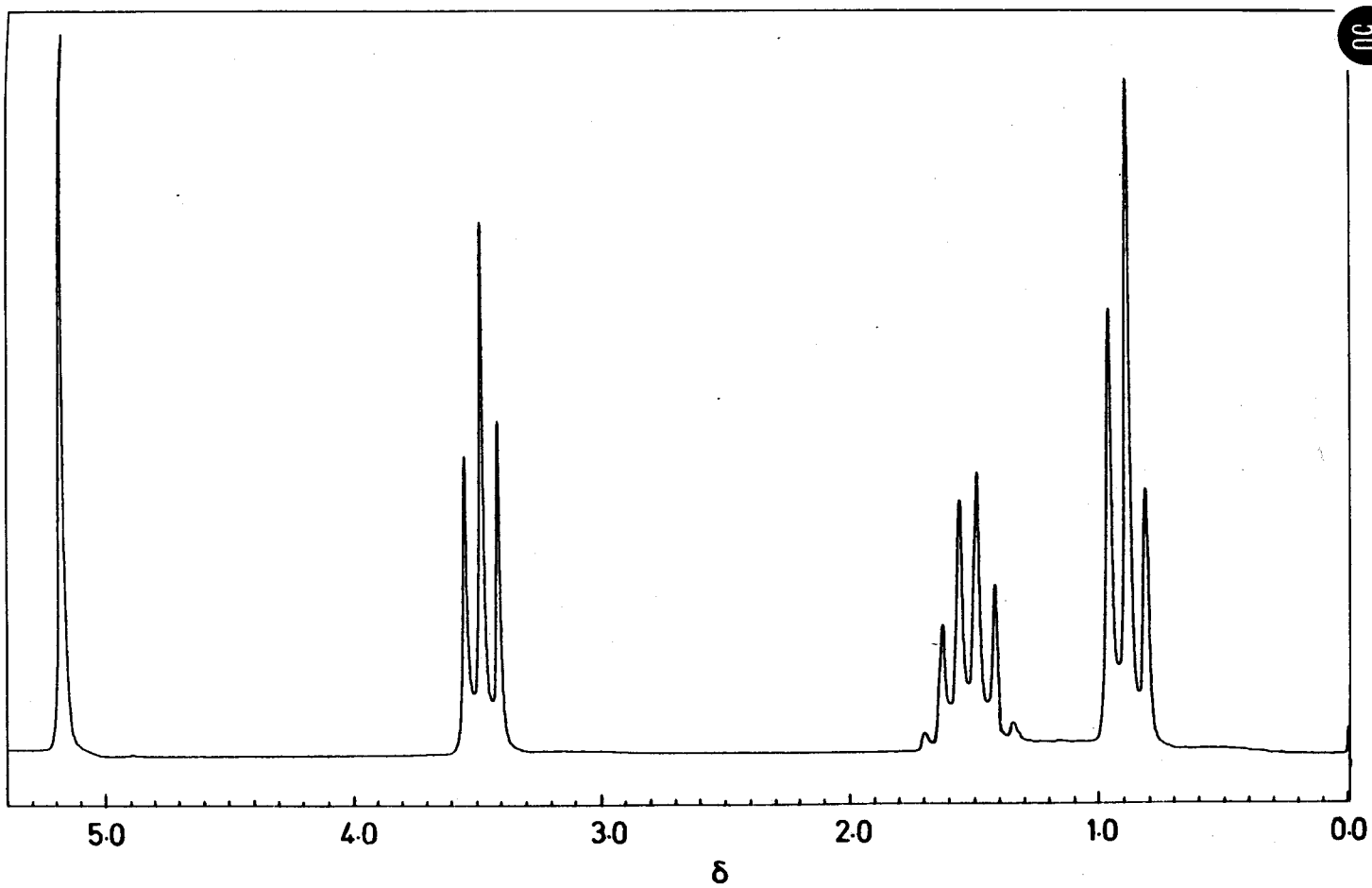
For $\delta_1-\delta_2 > J$ or $\sim J$, spectrum is referred to as 'AB' type

Examples

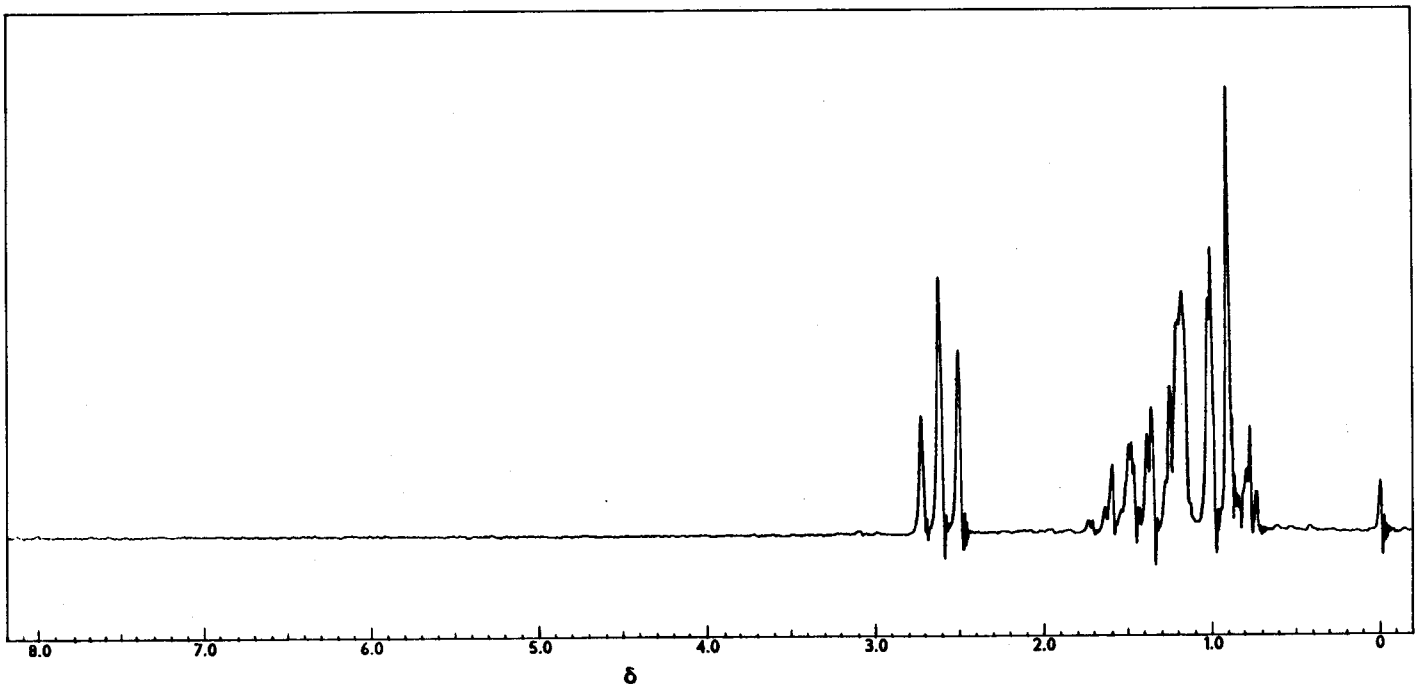
A_2X_3	CH_3CH_2Br	(FRAME 42)
AX_3	CH_3CHO	(FRAME 29)



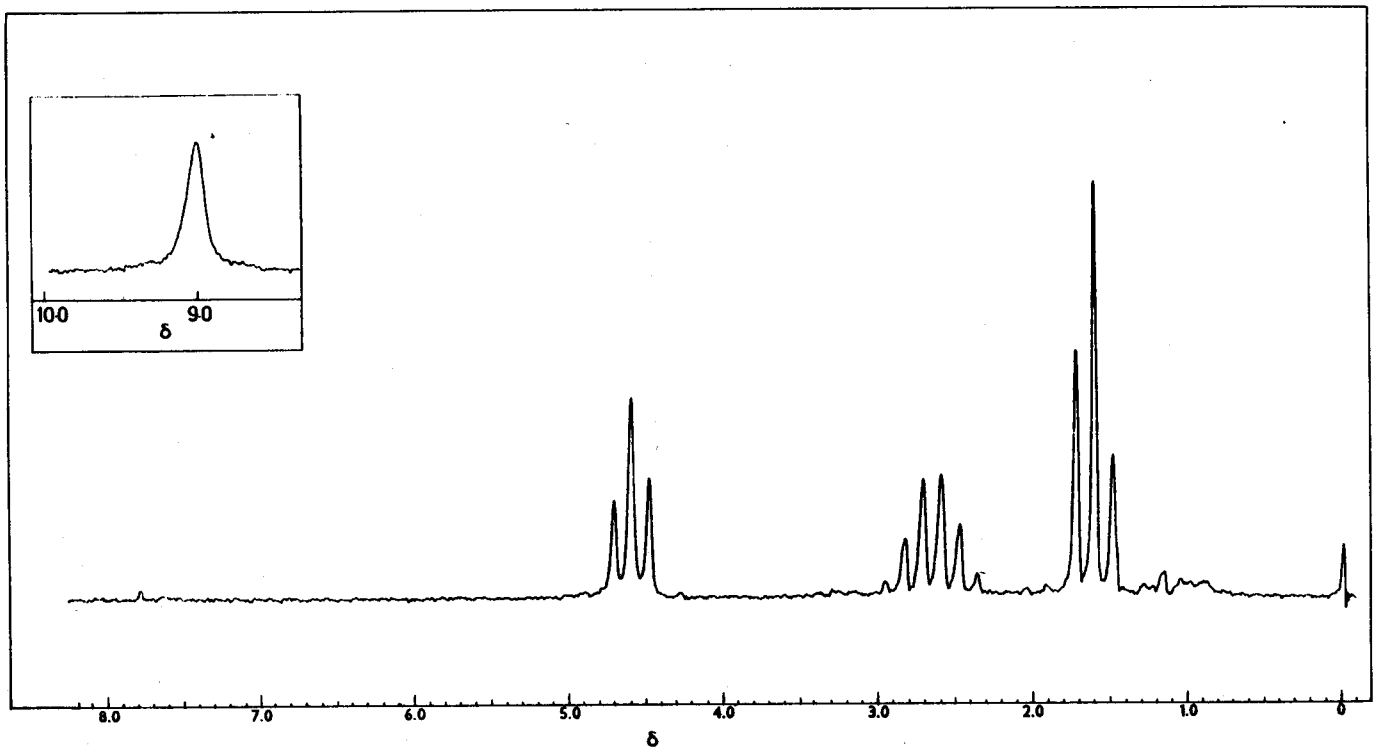
^{1}H n.m.r. spectrum of propan-1-ol, $CH_3CH_2CH_2OH$ (recorded at 60 MHz)



^{1}H n.m.r. spectrum of propan-1-ol (recorded at 100 MHz)



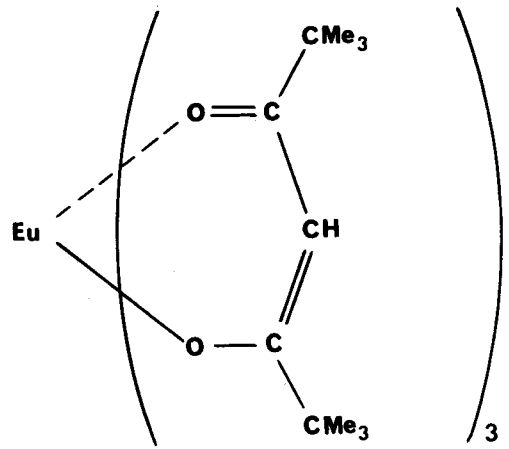
^{1}H n.m.r. spectrum of 1-aminopropane, $CH_3CH_2CH_2NH_2$ (recorded at 60 MHz)



^{1}H n.m.r. spectrum of 1-aminopropane in the presence of a shift reagent

53

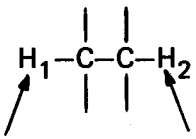
An example of a shift reagent



Tris(2,2,6,6-tetramethylheptane-3,5-dionato)europium

54

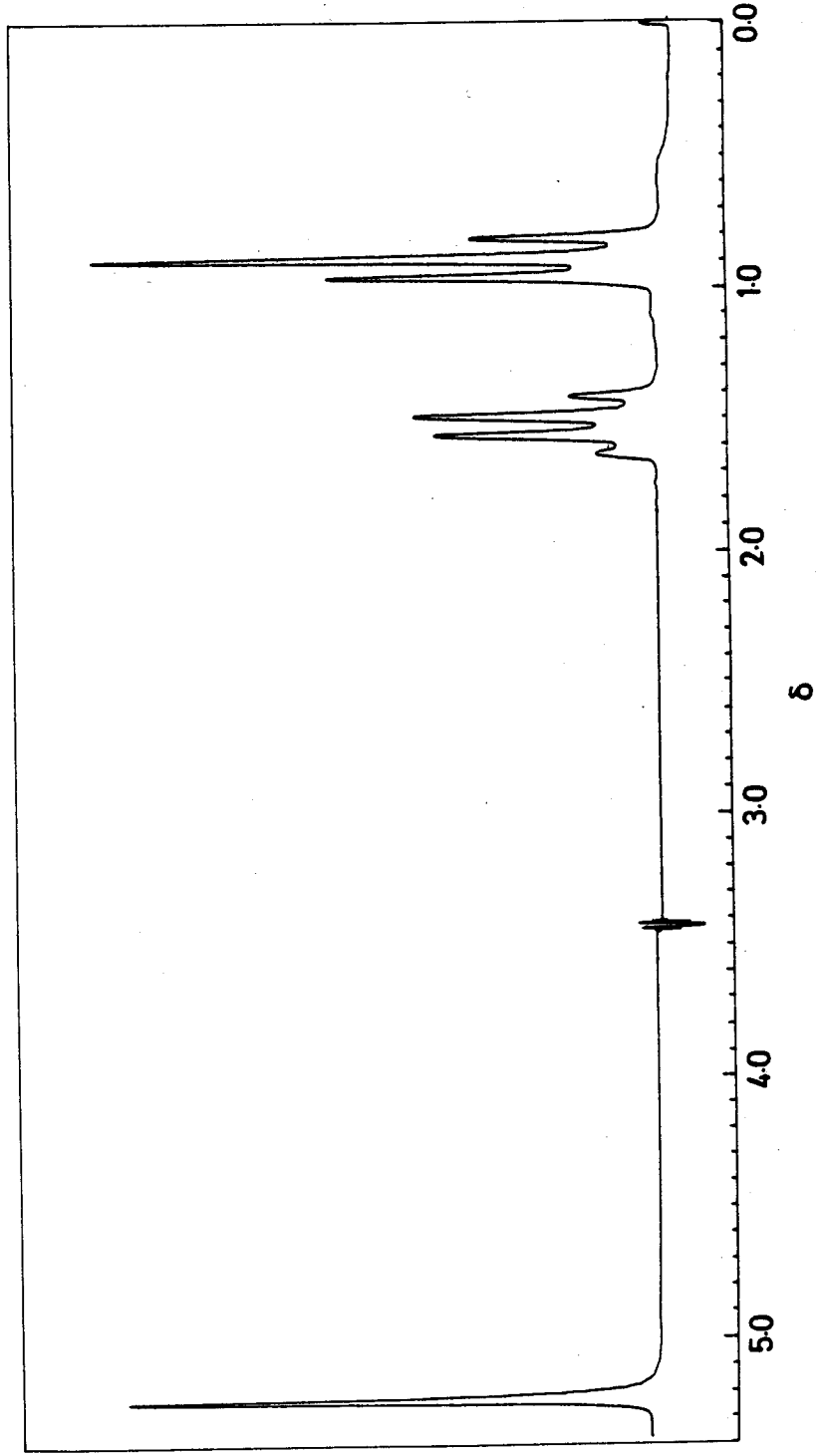
Basis of a *decoupling* experiment



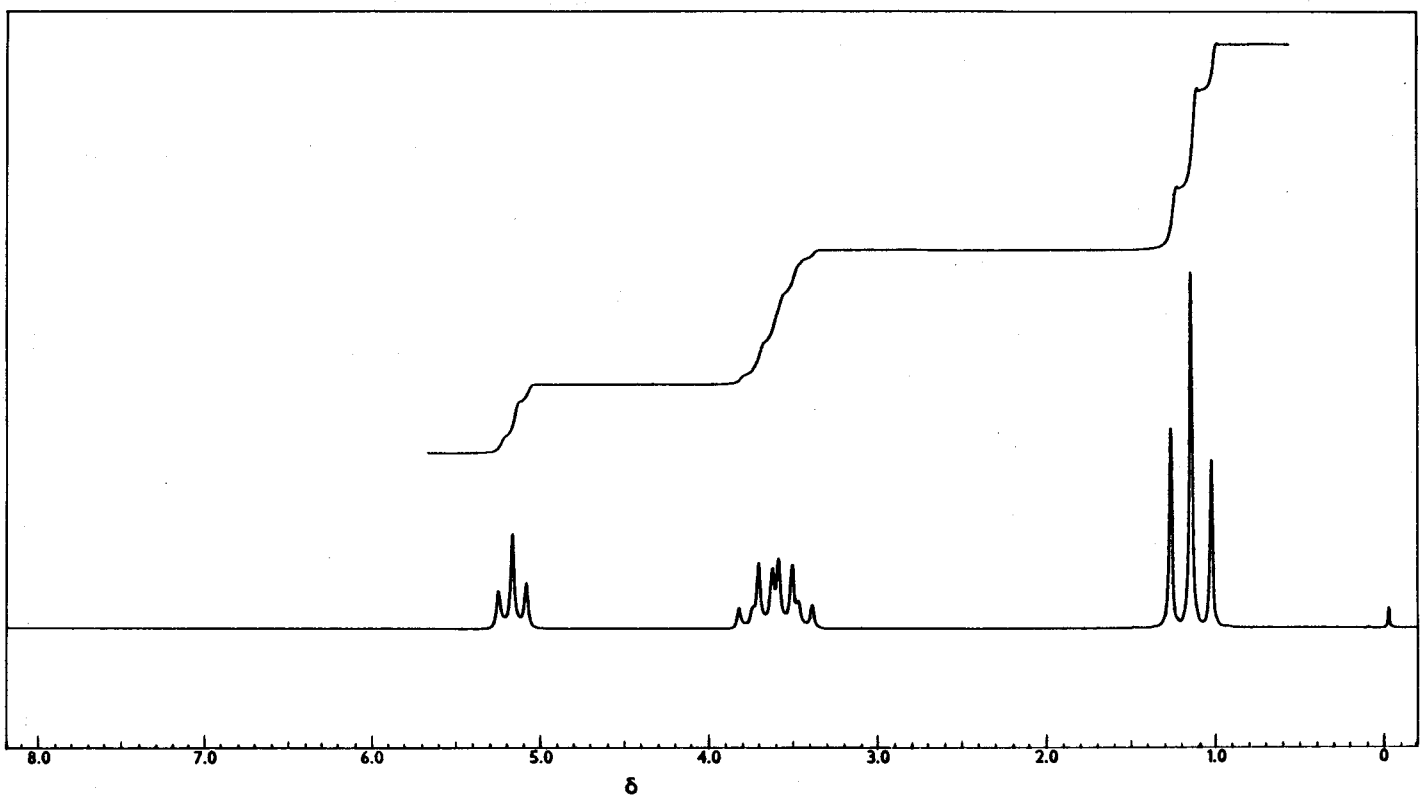
magnetic field adjusted for resonance of this proton

rapid transitions between the spin states for this proton induced by incident radiation of the appropriate frequency

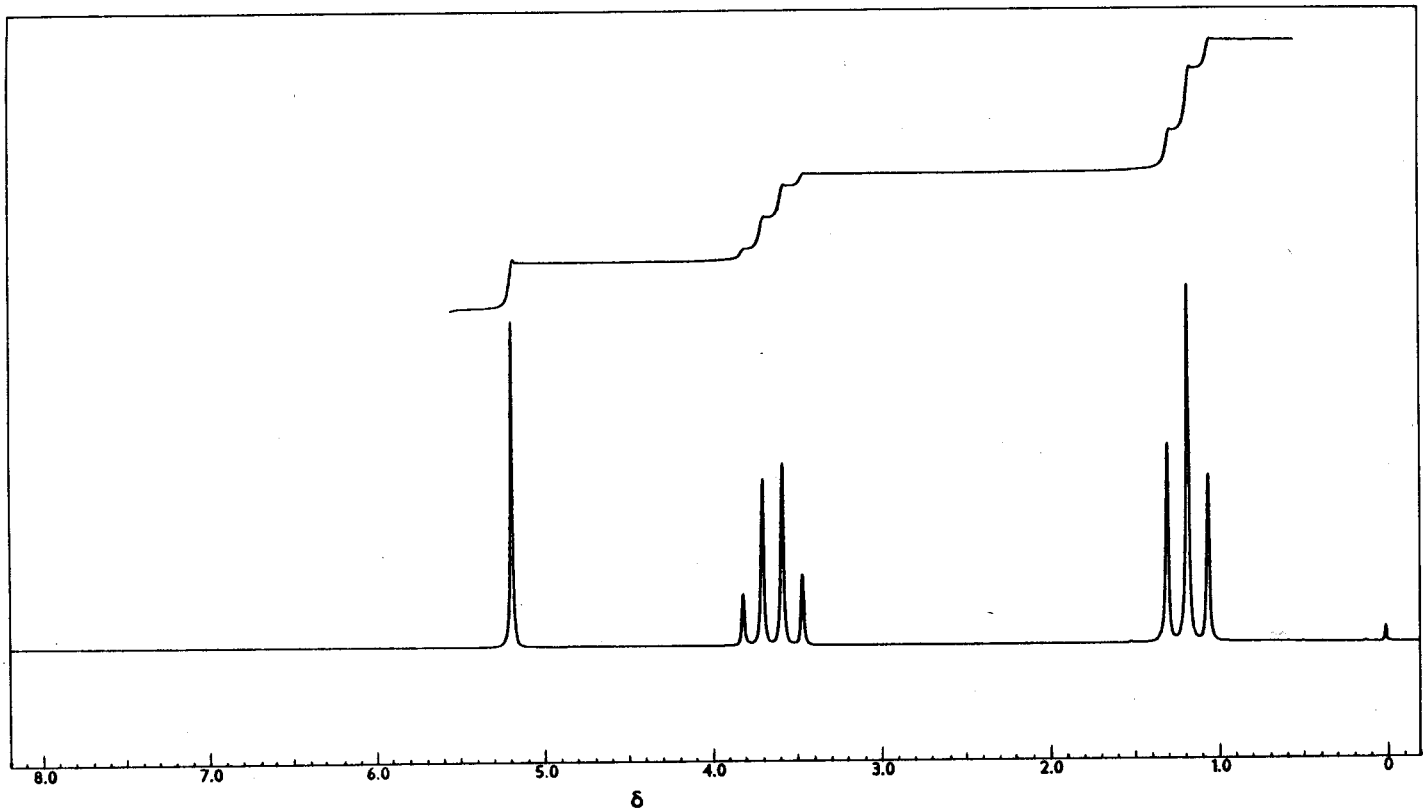
55



^{1}H n.m.r. spectrum of propan-1-ol recorded at 100 MHz with decoupling by simultaneous irradiation of the methylene protons at δ ca.3·5

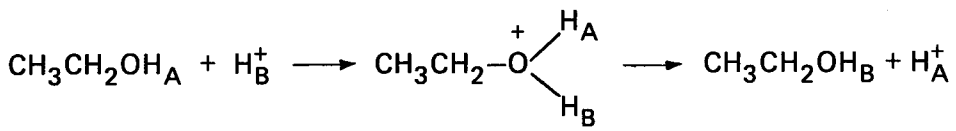


^{1}H n.m.r. spectrum of ethanol (rigorously purified)

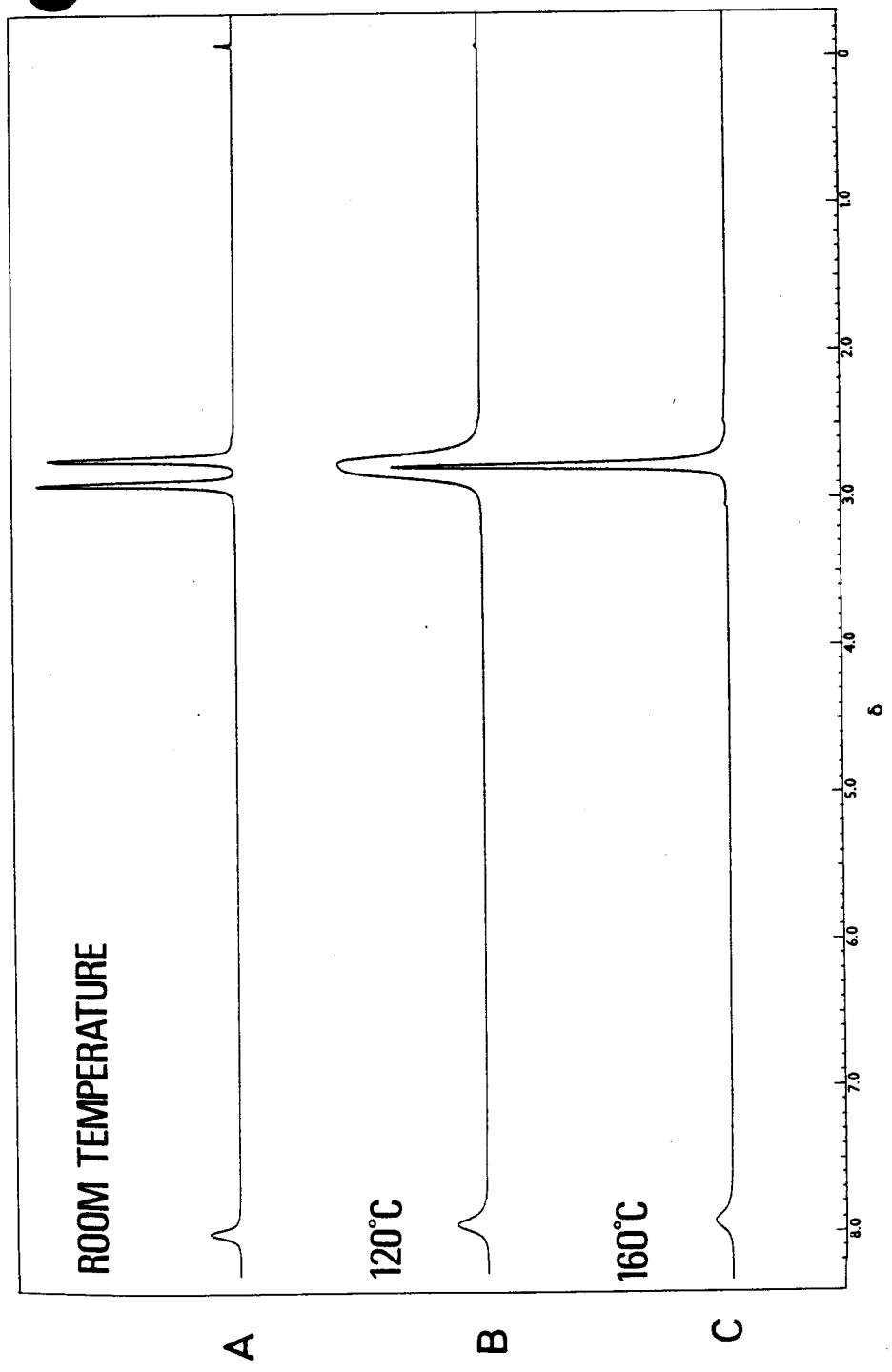


^{1}H n.m.r. spectrum of ethanol containing a trace of acid

58

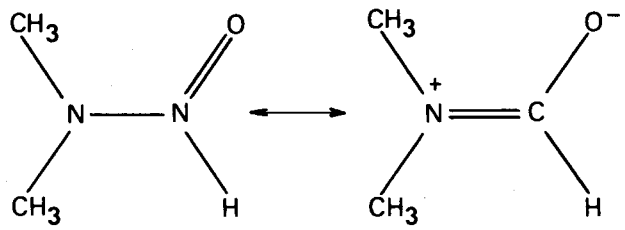


59

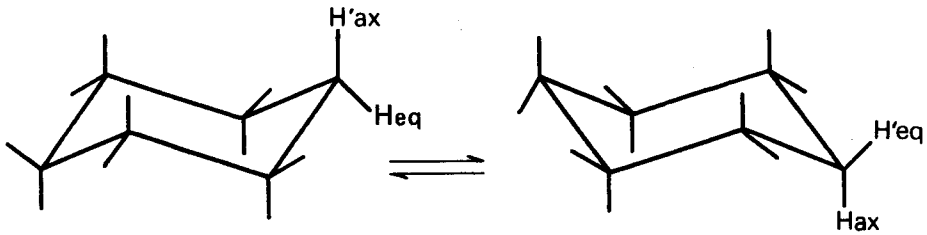


^1H n.m.r. spectrum of dimethylmethanamide, Me_2NCHO, recorded at three temperatures on a 60 MHz spectrometer

60



61



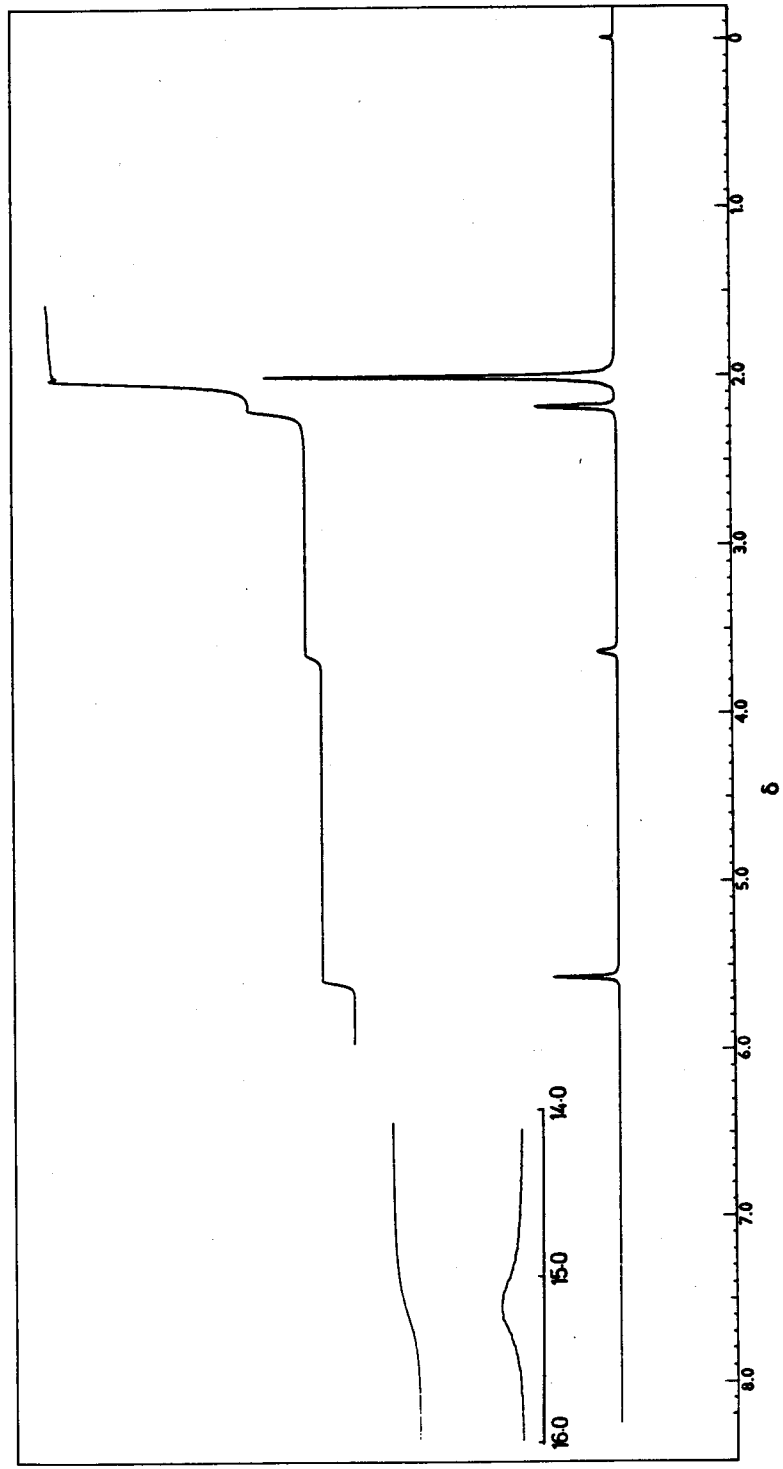
62

Rate of exchange at the coalescence point

$$= \sqrt{2}\pi\Delta\upsilon \ s^{-1}$$

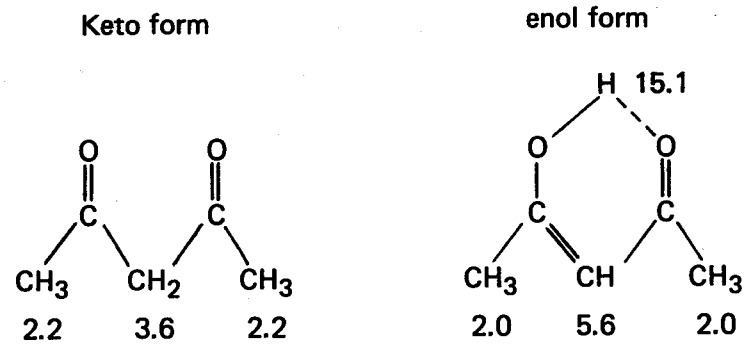
where $\Delta\upsilon$ is the frequency difference in Hz between the two absorptions in the slow-exchange spectrum

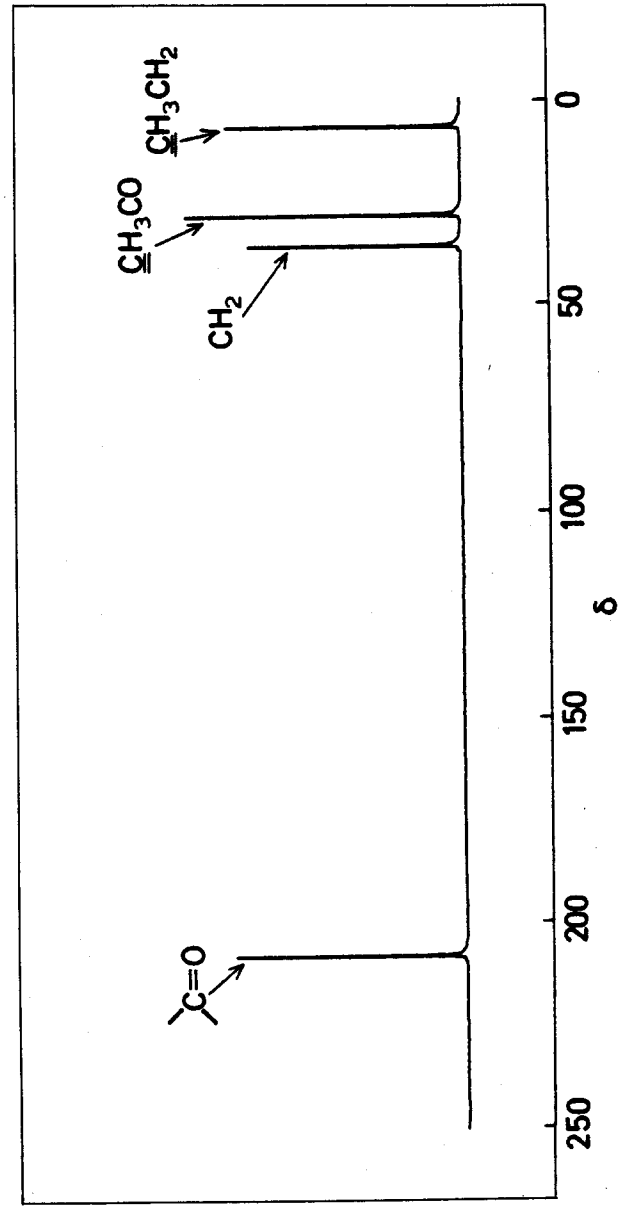
63



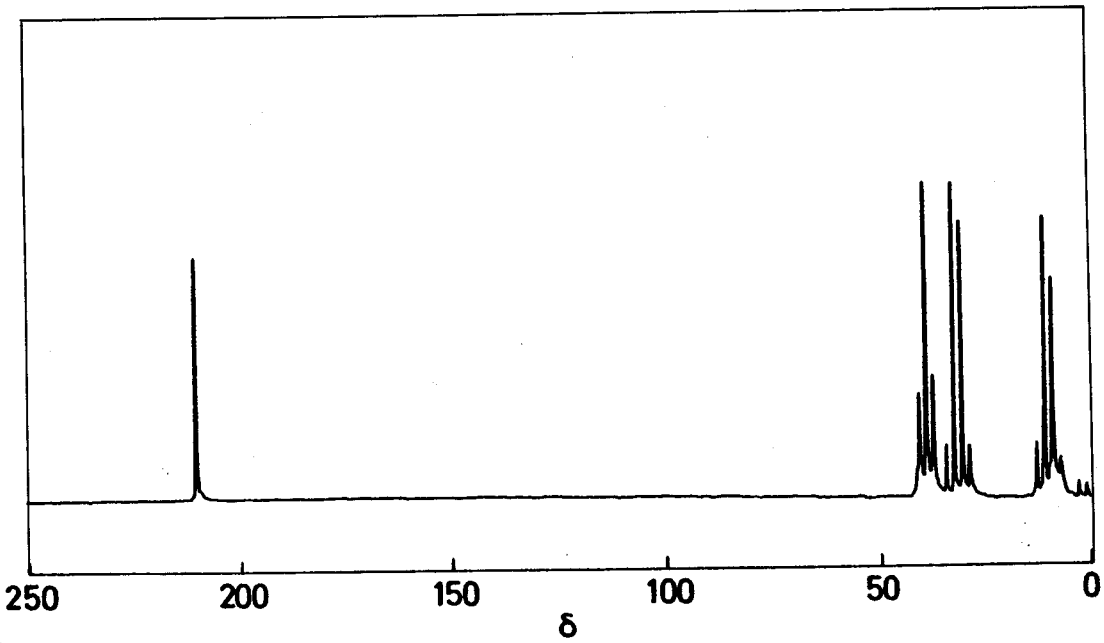
^{1}H n.m.r. spectrum of pentane-2,4-dione, $CH_3COCH_2COCH_3$

Tautomeric forms of pentane-2,4-dione

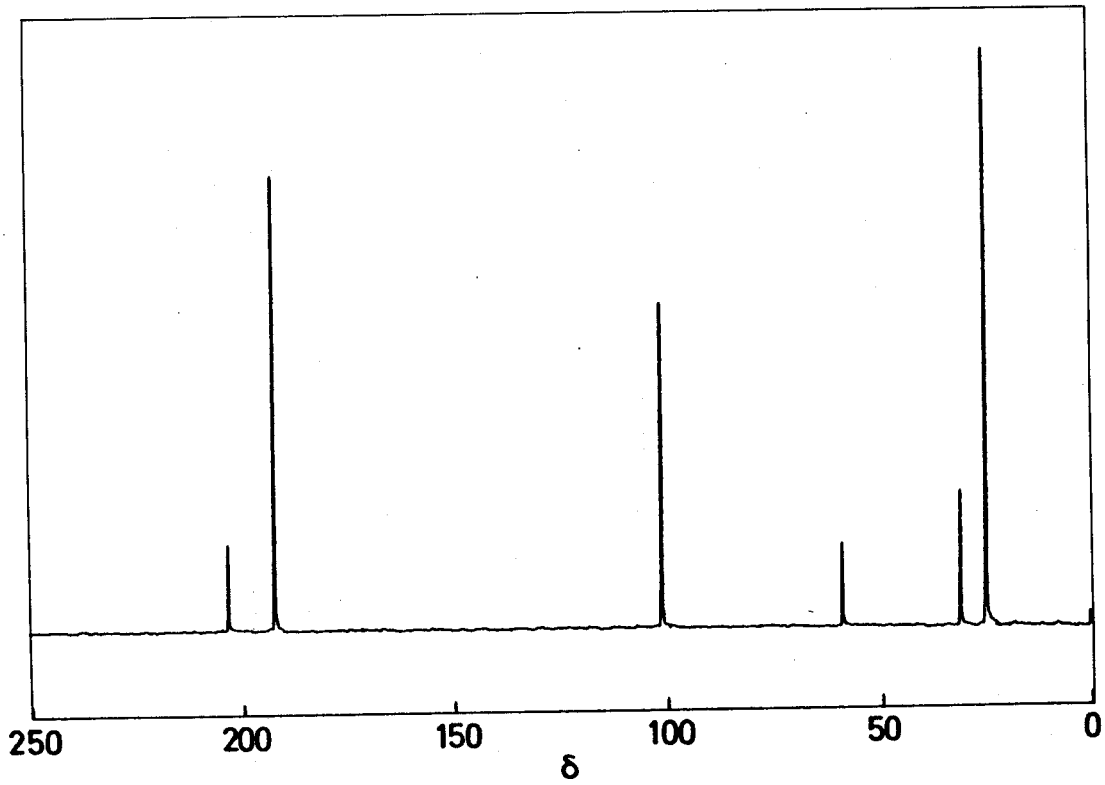




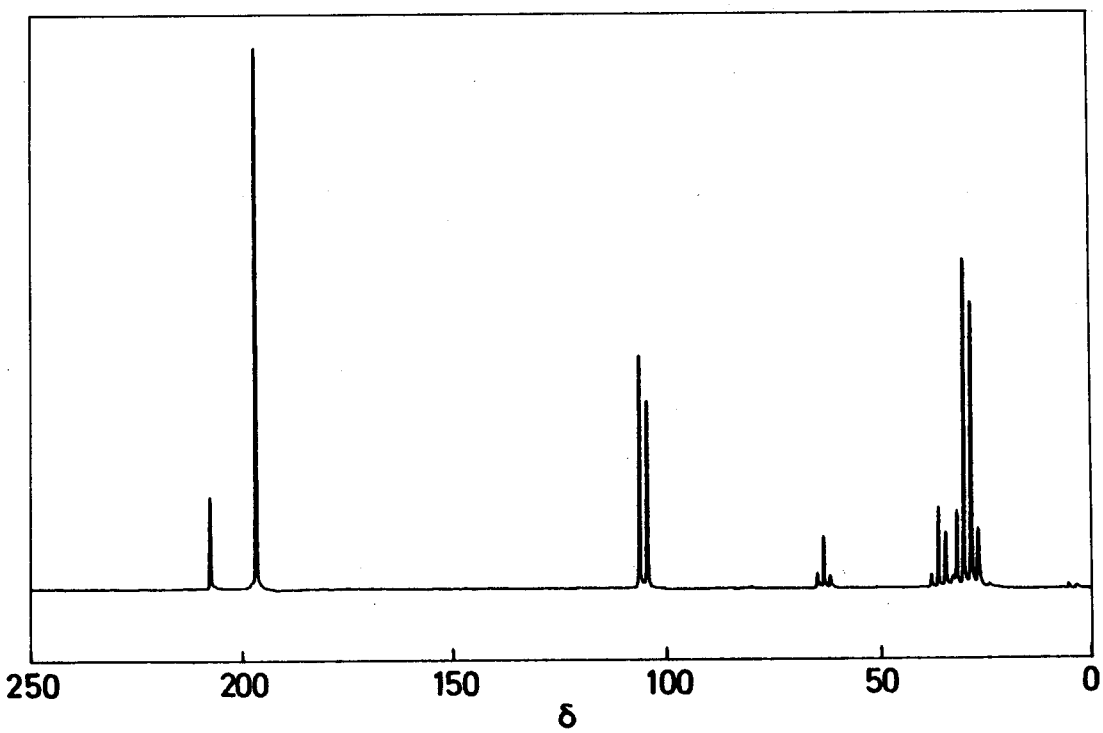
^{13}C n.m.r. spectrum of butanone, $CH_3COCH_2CH_3$ (proton decoupled)



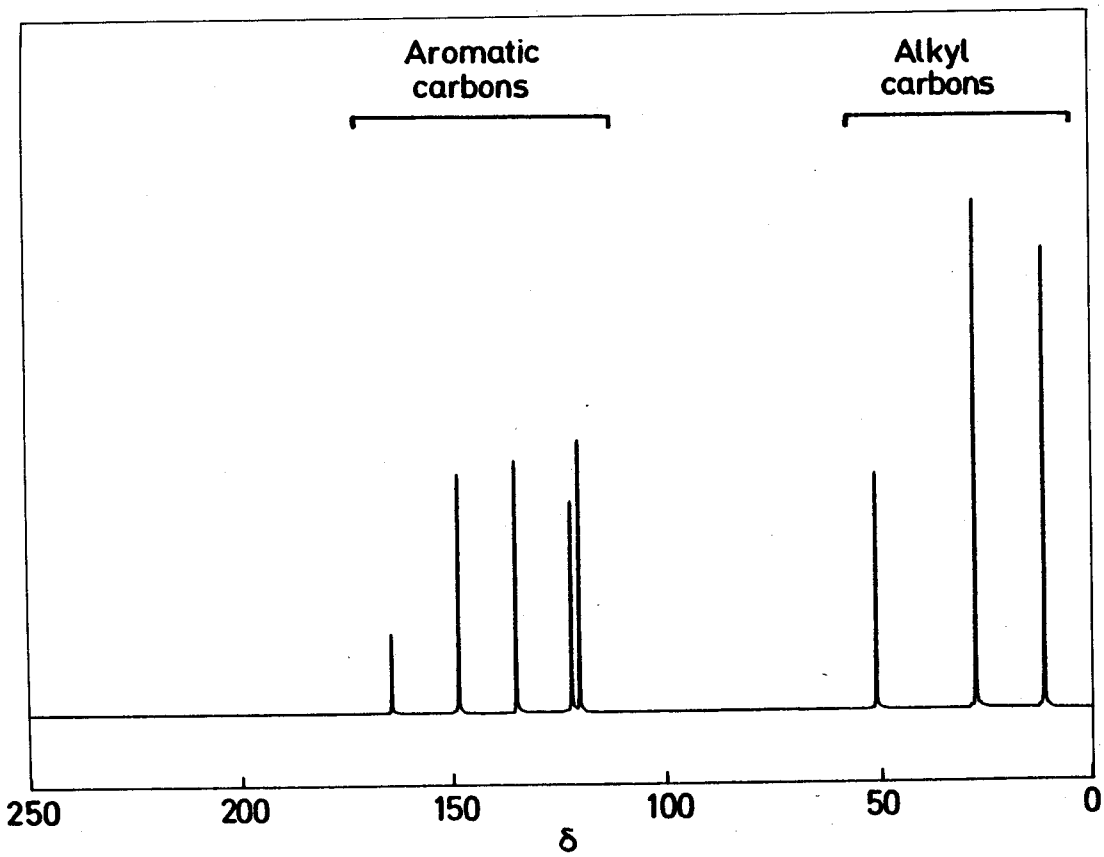
^{13}C n.m.r. spectrum of butanone, partially decoupled ('off-resonance' decoupling)



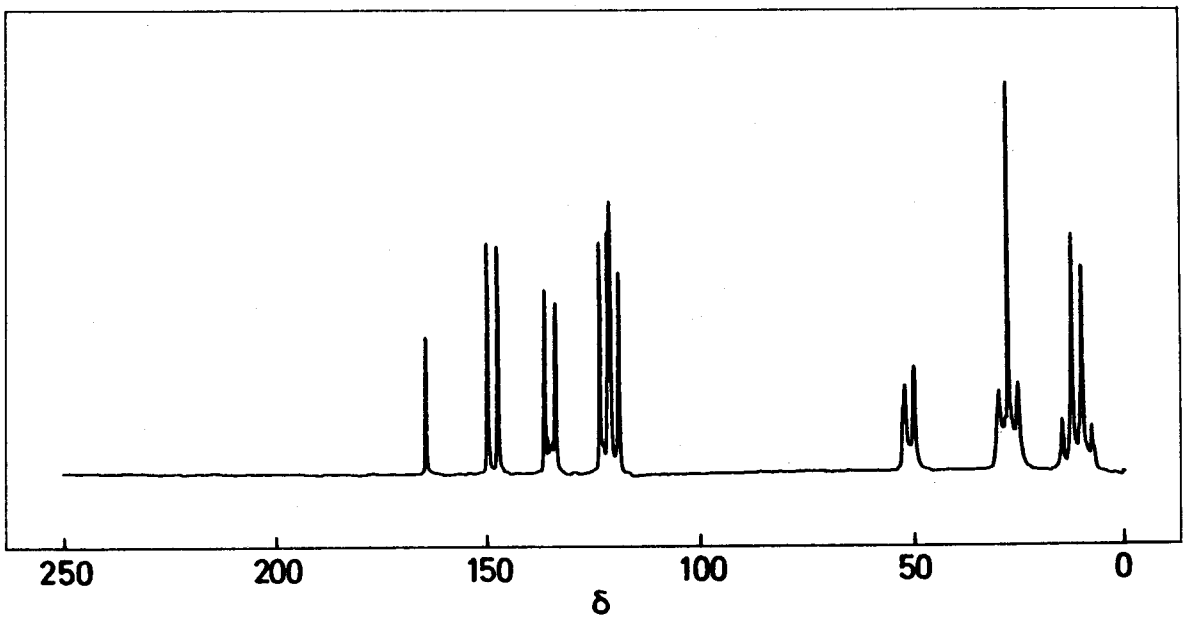
^{13}C n.m.r. spectrum of pentane-2,4-dione (proton decoupled)



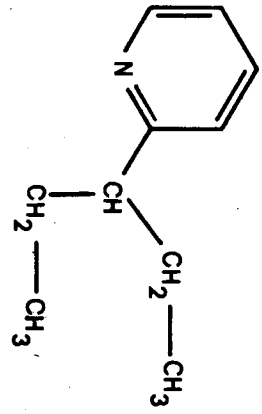
^{13}C n.m.r. spectrum of pentane-2,4-dione ('off-resonance')



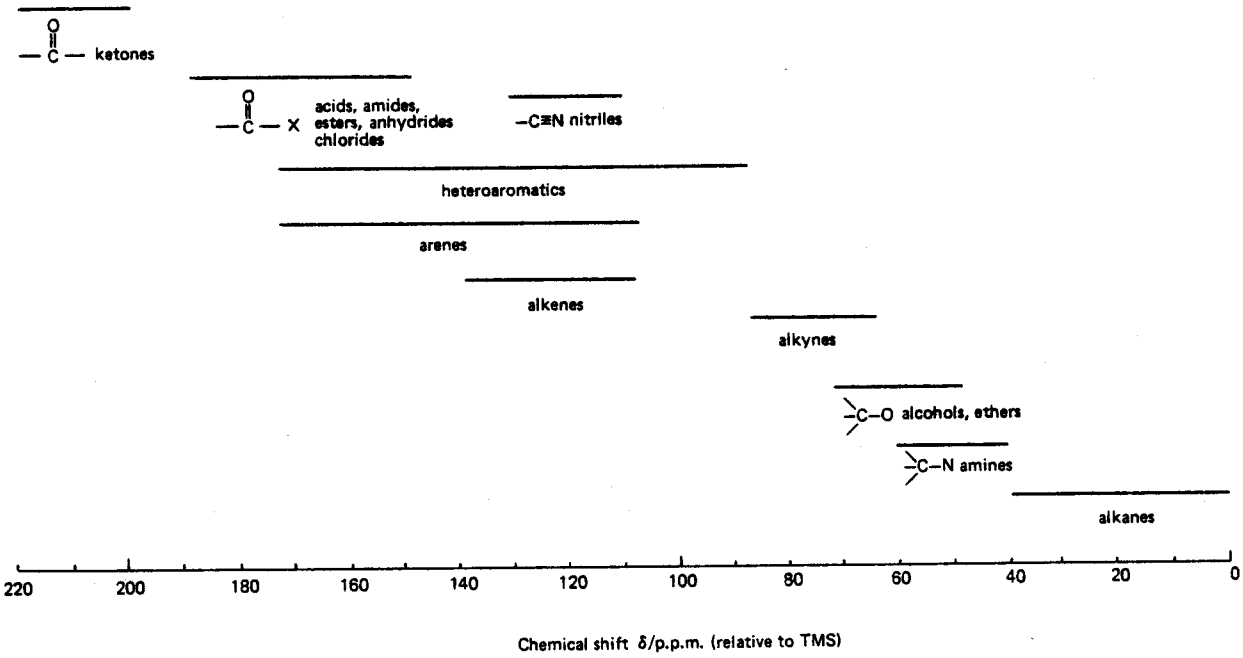
^{13}C n.m.r. spectrum of 2-(1-ethylpropyl)pyridine (proton decoupled)

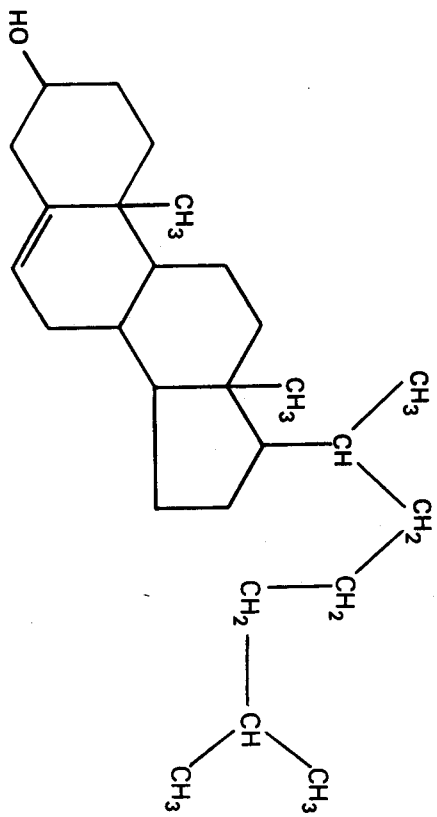


^{13}C n.m.r. spectrum of 2-(1-ethylpropyl)pyridine ('off-resonance')



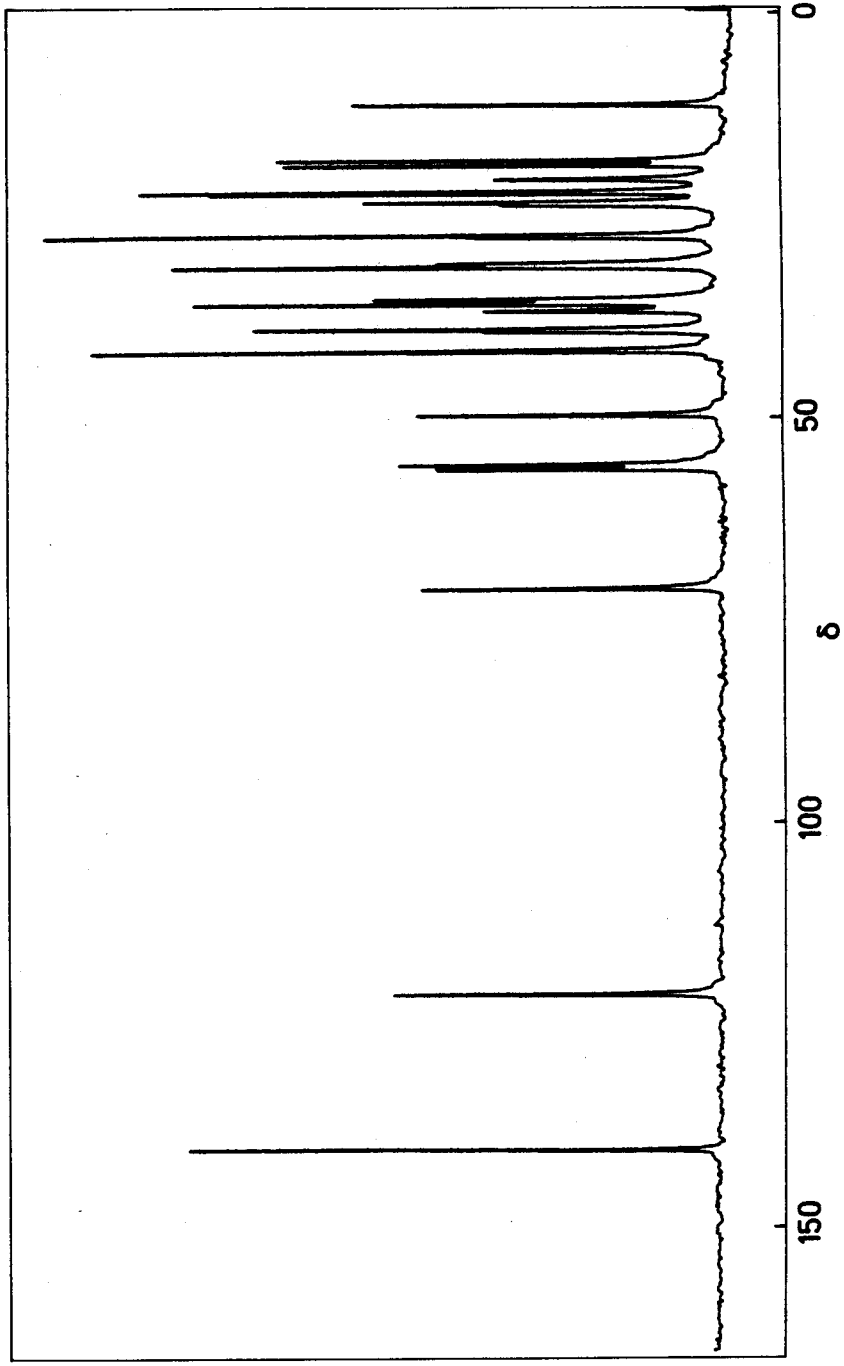
TYPICAL RANGES OF ^{13}C CHEMICAL SHIFTS





Cholesterol

74

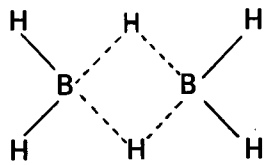


^{13}C n.m.r. spectrum of cholesterol (proton decoupled)

75

^{11}B n.m.r. spectrum of diborane, B_2H_6

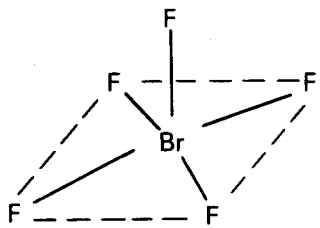
76



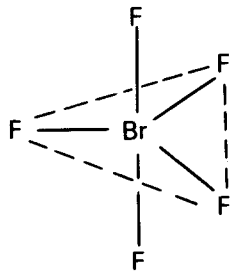
The structure of diborane, B_2H_6

77

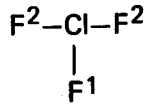
A



B

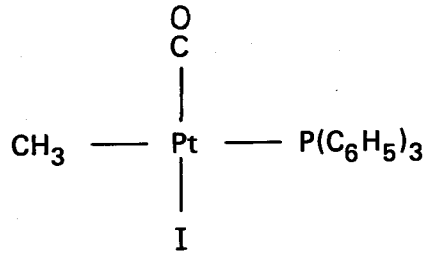


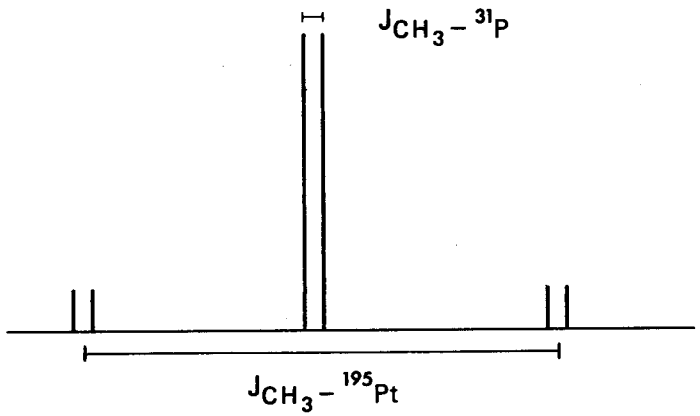
78



The structure of chlorine trifluoride, ClF_3

79





^1H n.m.r. spectrum of the methyl-group protons in $Pt(CH_3)(I)(CO)[P(C_6H_5)_3]$.

The intense doublet is the spectrum from molecules which contain those Pt isotopes which do not possess a magnetic moment; there is a doublet splitting from interaction with ^{31}P.

The small 'satellite lines' are from those molecules which contain ^{195}Pt (present in 33% natural abundance) and show splitting into two doublets [from interaction with ^{31}P and ^{195}Pt ($I = ½$)]

Appendix 1

Table of chemical shifts (δ) for protons in organic molecules*†

CH_3-C	saturated alkyl group	0.9	$HC\equiv C-$	alkyne, unconjugated	1.8
$C-CH_2-C$	saturated alkyl group	1.3		alkyne, conjugated (to C=C, C=O, Ar, etc.)	2-3
$C-CH(C)-C$	saturated alkyl group	1.5			
$CH_3-C=C$	alkene	1.7	$H-C=C$	alkene, unconjugated	4.7-5.5
CH_3-Ar	arene	2.2		alkene, conjugated (to C=C, C=O, etc.)	4.5-8.0
$CH_3-C(=O)-O$	ester, acid	2.0	H-(benzene)	benzene	7.3
$CH_3-C(=O)-$	ketone, alkanal	2.1	H-(R-benzene)	substituted benzene	6.5-8.5
CH_3-N	amine	2.2	H–Ar	heteroaromatic	6.0-8.5
CH_3-O-	methyl ether	3.3	$H-C(=O)-$	alkanal	9.6-9.9
$CH_3-O-C(=O)-$	methyl ester	3.7	$H-O-C(=O)-$	carboxylic acid	10-13
CH_3-I	iodomethane	2.2			
CH_3-Br	bromomethane	2.7	H–O–R	alkanol	‡
CH_3-Cl	chloromethane	3.0	H–N	amine	‡
CH_3-F	fluoromethane	4.3			
CH_3NO_2	nitromethane	4.4			

* Typically ± 0.1 δ unless indicated otherwise.

† Methylene (CH_2) and methine (CH) hydrogens generally have somewhat higher δ values than a methyl group in a similar environment, cf. the behaviour of saturated alkyl groups.

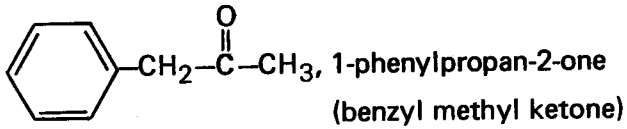
‡ Peaks often broad; δ values may vary considerably with concentration and solvent.

Appendix 2

Answers to Problems

1 $Me_2CH{-}O{-}CHMe_2$, bis(1-methylethyl)ether

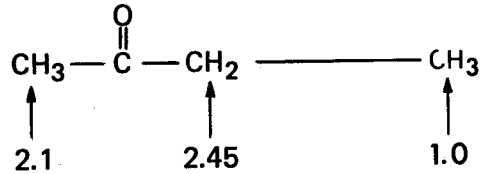
2 $CH_3CH_2CH_2NO_2$, nitropropane. Note here that the methylene group adjacent to the methyl group interacts with *five* adjacent protons in the neighbouring methyl and methylene groups. Thus a 1:5:10:10:5:1 pattern results.

3 

, 1-phenylpropan-2-one (benzyl methyl ketone)

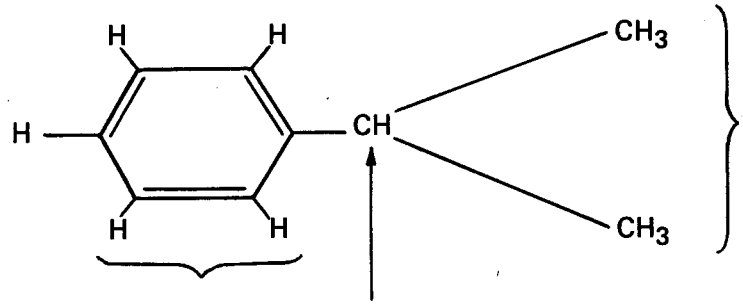
Analysis of the ^1H n.m.r. spectra of the worked examples

Butanone (methyl ethyl ketone), see *Frame 35*



Chemical shift / δ:	2.1	2.45	1.0
splitting pattern :	no splitting	1:3:3:1 (from 3 adjacent methyl-group protons)	1:2:1 (from 2 adjacent methylene-group protons)

(1-Methylethyl)benzene (Cumene), see *Frame 39*



Chemical shift / δ:	7.1 (all 5 aromatic protons)	2.75 (single proton)	1.15 (six equivalent protons from the two methyl groups)
splitting pattern :	no splitting	1:6:15:20:15:6:1 (from the 6 adjacent methyl-group protons)	1:1 (from the single adjacent proton)

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