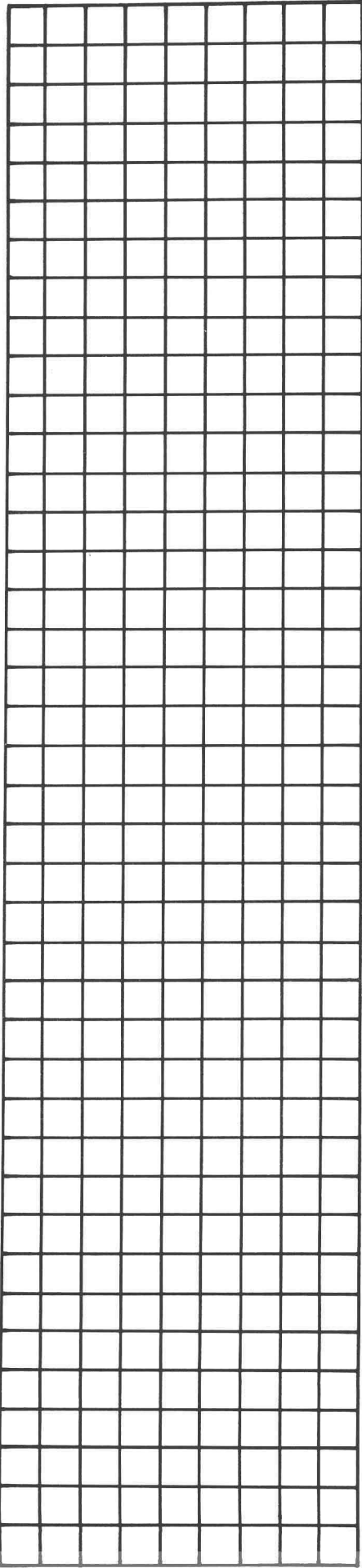


THE SADTLER GUIDE TO CARBON-13 NMR SPECTRA

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Published by
Sadtler Research Laboratories
Division of Bio-Rad Laboratories, Inc.
3316 Spring Garden Street
Philadelphia, Pennsylvania 19104

ISBN 0-8456-0087-7

Library of Congress Catalog Card Number: 82-050006

Co-published for exclusive distribution in Europe by
Heyden & Son Ltd.
Spectrum House, Hillview Gardens
London N.W. 4, England 2JQ

ISBN 0-85501-550-0

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Printed in the United States of America

**THE SADTLER
GUIDE TO
CARBON-13 NMR
SPECTRA**

CHEMICAL CLASSIFICATION IN ALPHABETICAL SEQUENCE

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Arenes	51	63
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Disulfides	316	381
Esters	471	569
Ethers	334	403
Fluorinated Hydrocarbons	77	91
Iodinated Hydrocarbons	110	135
Ketones	388	463
Nitriles	255	303
Nitro Compounds	272	325
Oximes	244	289
Phosphorus Compounds	283	339
Primary Amides	426	511
Primary Amines	127	155
Pyridines	197	235
Quaternary Ammonium Salts	235	277
Secondary Amides	431	519
Secondary Amines	148	179
Sulfides	305	367
Sulfones	322	389
Tertiary Amides	439	529
Tertiary Amines	168	203
Thiocyanates	269	321
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INTRODUCTION

The Sadtler Guide to Carbon-13 NMR Spectra is a survey collection of 500 specially selected carbon-13 NMR spectra that parallels the Sadtler PMR guides published previously ⁽¹⁾. The purpose of this volume is to present high quality spectra backed by comprehensive chemical shift tables and additivity data for the evaluation and interpretation of carbon spectra, as a learning experience for the novice and as an aid in the analysis and characterization of molecular structures.

The chemical shift assignments are as sufficiently detailed and comprehensive as possible so that they can be used effectively by the experienced chemist and spectroscopist. The spectra are presented in a format which, it is hoped, will be useful to the undergraduate and laboratory technician who will find these typical spectra helpful in pattern recognition.

The ordering system by functional groups is similar to that employed in the Sadtler handbook series that cover the areas of IR, PMR and UV spectroscopy and follows the progression of compound types that is used in most organic chemistry texts.

The emphasis of the text and tables is on the chemical shifts exhibited by the groups of spectra as determined by the shielding or deshielding effect of the functional groups under discussion. For those desiring a detailed treatment of carbon-carbon and heteronuclear coupling constants or relaxation time studies, reference should be made to current texts which cover these areas in some detail ⁽²⁾.

The spectra were determined on either a Varian CFT-20 FTNMR system at ambient temperature (36°C) utilizing 10 mm tubes and a deuterium internal lock or on a Varian HA-100/Digilab FT-NMR-3 system at ambient temperature (31°C) using 8 mm NMR tubes with an external fluorine lock.

Tetramethylsilane (TMS) was used as the primary internal reference with p-dioxane being used with D₂O solutions. For chemical shift conversion purposes, the p-dioxane peak was taken as 67.4 ppm, while all other chemical shifts were referenced to TMS. The solvents predominantly used in preparing the spectra were CDCl₃, H₂O, D₂O, DMSO-d₆ (deuterated dimethyl sulfoxide) or polysol-d (50% CDCl₃/50% DMSO-d₆).

Due to the importance of solvent effects on carbon chemical shifts, all tabulated data list the solvent used to prepare the spectrogram. The carbon-13 shieldings of some common solvents and reference materials are shown on the following page ⁽³⁾.

- (1) a. The Sadtler Guide to NMR Spectra (Proton), Sadtler, Philadelphia, 1972.
- b. The Sadtler Guide to NMR Spectra of Polymers, Sadtler, Philadelphia, 1973.
- (2) a. Breitmaier and Voelter, 13-C NMR Spectroscopy, Verlag Chemie, Weinheim, 1974.
- b. Levy, Lichter and Nelson, Carbon-13 Nuclear Magnetic Resonance Spectroscopy, 2nd edition, Wiley-Interscience, New York, 1980.
- c. Memory and Wilson, NMR of Aromatic Compounds, Wiley-Interscience, New York, 1982.
- d. Wehrli and Wirthlin, Interpretation of Carbon-13 NMR Spectroscopy, Heyden, London, 1980.
- (3) J. B. Stothers, Carbon-13 NMR Spectroscopy, Table 2.2, p. 49, Academic Press, Inc., New York, 1972.

Compound	ppm from TMS
carbon disulfide	193.7 (external) 192.8 (internal)
benzene	128.7 (concentration dependent)
carbon tetrachloride	96.0
chloroform	77.2
p-dioxane	67.4 (concentration dependent)
dimethyl sulfoxide	40.4 (concentration dependent)
cyclohexane	27.7
methyl iodide	20.5 (temperature dependent)

The structural formula is shown on each spectrum with annotations corresponding to the assigned chemical shift values for each carbon atom. The remaining instrumental data listed shows the solvent, the reference, and the scale offset value for any nuclei which resonate at frequencies lower than TMS or higher than 200 ppm.

The chemical shifts of the carbon nuclei observed in the spectrum have been assigned to specific carbons in the molecular structure. These assignments have been made using literature reference data when available and chemical shift data from similar structural fragments.

All assignments made without a fair degree of confidence are indicated by an asterisk (*) and noted as tentatively assigned. Also, when assignments can be classified as "either" - "or" the assignment is given followed by a slash (/) and reference to the other nucleus in question.

EXAMPLE

A	14.1
B	22.7
C	31.4/d
D	31.8/c

Any impurities which show in the spectrum are indicated in the assignments section by the abbreviation "imp".

Carbon-13/heteroatom coupling constants, when observed in a spectrum, are printed at the end of the assignments section.

EXAMPLE

$$J_{^{19}\text{F}-\text{C}} = 26 \text{ Hz}$$

In order to define simple molecular structures in a linear format suitable for typing, several shorthand notations are used throughout the text. Standard chemical notations are employed with the three additions described on the following page.

C_n — is used to describe an alicyclic ring containing “n” carbon atoms, where C₃ represents cyclopropane, C₄ represents cyclobutane, etc.

R_n — is used to define normal (straight chain) alkyl groups consisting of “n” number of carbons, so that R₄ — represents a butyl group and R₁₂ — describes a dodecyl group. The letter R is occasionally used without a numerical subscript, in which case it represents a branched or unspecified aliphatic group in which branching or other substituents are not considered to have a pronounced effect upon the chemical shifts of the proton group under examination.

Ø — is used to represent a phenyl group or a substituted benzene ring with additional substituents shown in brackets, i.e. — Ø(3-Cl,4-NO₂).

Examples of notation system:

R₉—Ø would represent a nonyl benzene or a derivative of nonyl benzene,

R₂—NH—C(=S)—NH₂ describes N-ethyl thiourea,

CH₃—C(=O)—O—CH₂CH(R₂)—R₄ would indicate acetic acid, 2-ethyl hexyl ester, and

C₅—Cl would represent chlorocyclopentane.

With each chemical shift table two spectrum numbers are provided. The first one titled “Sadtler Ref.” indicates the spectrum number of the compound in the Sadtler Standard Carbon-13 NMR Spectra which, as of 1982, contains 14,000 spectrograms. The second column titled “Book Number” refers to the number of the spectrogram in this text.

As the combination of proton and carbon-13 NMR becomes the primary analytical technique in many fields of structural elucidation, the need for reliable tabulated carbon-13 NMR data becomes acute. It is hoped that this guide to carbon-13 NMR spectra will supplement the scattered data available in the current literature.

All spectra in this text are indexed numerically, alphabetically and by molecular formula to provide rapid location and identification.

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THE ALKANES

This section contains the carbon-13 spectra of the straight chain and branched alkanes. The spectra of substituted derivatives will be found in the section of this text devoted to the spectra containing that substituent. For example, the spectrogram of decylamine is spectrum number 129 and is located with the spectra of the primary amines.

The aliphatic additivity constants presented in many of the section heading discussions are usually very useful when utilized with these parent alkane chemical shifts in the calculation of theoretical chemical shifts for straight and branched aliphatic compounds. Texts such as *Carbon-13 NMR Spectra*, F. W. Wehrli and T. Wirthlin, Heyden, Philadelphia (1980), provide a good overview of the recent literature on the additivity of carbon-13 chemical shifts.

THE ALKANES								<u>Solvent</u>	<u>Sadtler Ref.</u>	<u>Book Number</u>
C-7	C-6	C-5 CH ₃ -	C-4 CH ₂ -	C-3 CH ₂ -	C-2 CH ₂ -	C-1 -CH ₃				
		14.2	22.8	34.8	22.8	14.2	Pentane	CDCl ₃	1830C	—
	14.2	23.0	32.1	32.1	23.0	14.2	Hexane	CDCl ₃	126C	1
14.1	23.1	32.4	29.5	32.4	23.1	14.1	Heptane	CDCl ₃	414C	2
R2-	32.3	29.8	29.8	32.3	23.1	14.1	Octane	CDCl ₃	331C	—
R5-	30.1	30.1	29.7	32.3	23.0	14.2	Undecane	CDCl ₃	724C	—
R12-	29.9	29.9	29.6	32.2	22.9	14.2	Octadecane	CDCl ₃	316C	3

2-METHYL ALKANES

C-7	C-6	C-5	C-4 CH ₃ -	C-3 CH ₂ -	C-2 CH-	C-1 -(CH ₃) ₂				
			11.8	32.0	30.1	22.3		CDCl ₃	1831C	4
	14.1	23.2	29.9	39.0	28.2	22.7		CDCl ₃	3507C	—
14.2	23.0	32.5	27.3	39.3	28.3	22.8		CDCl ₃	9010C	10
R2-	32.3	29.9	27.7	39.4	28.3	22.8		CDCl ₃	8910C	—

3-ETHYL ALKANES

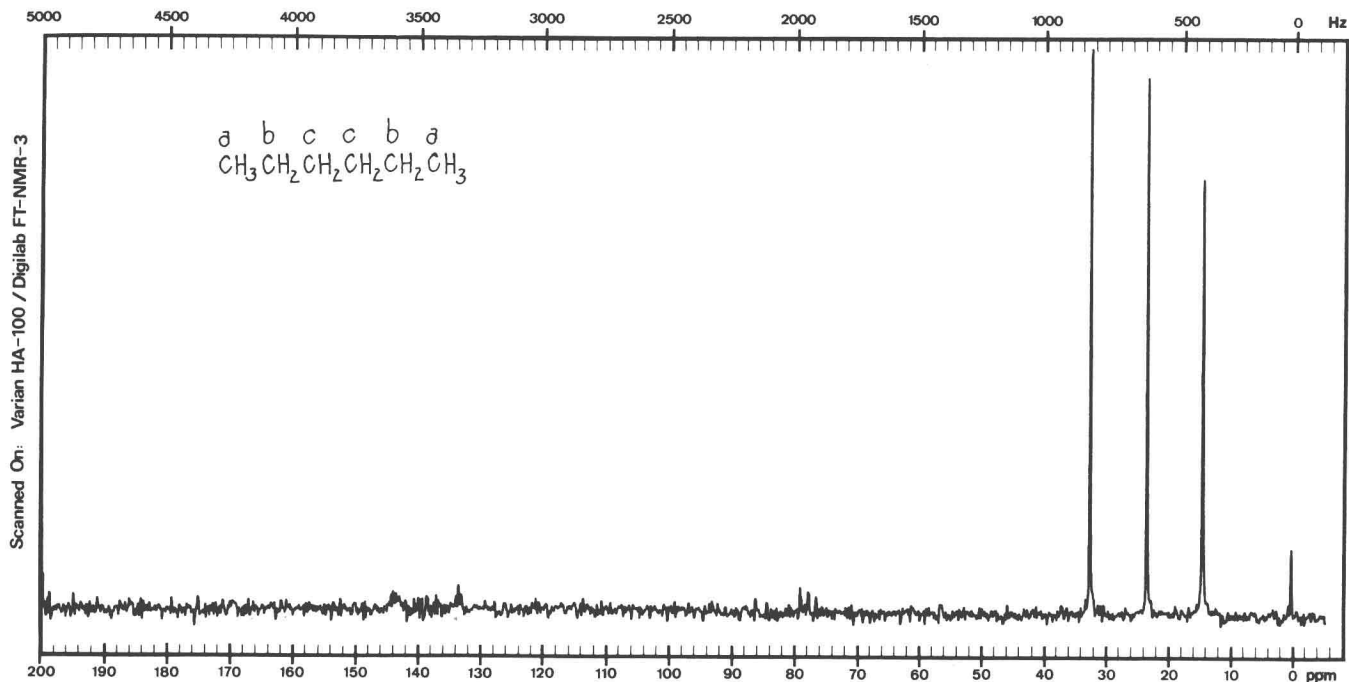
C-7	C-6	C-5	C-4 CH ₃ -	C-3 CH-	C-2 (CH ₂ -	C-1 -CH ₃) ₂				
			18.9	36.6	29.5	11.6		CDCl ₃	1829C	5
		11.1	25.5	42.5	25.5	11.1		CDCl ₃	6971C	6
14.2	23.4	29.3	32.8	40.7	25.7	11.0		CDCl ₃	9146C	12

2,2-DIMETHYL ALKANES

C-7	C-6	C-5	C-4	C-3	C-2	C-1
			CH ₃ -	CH ₂ -	C	-(CH ₃) ₃
			8.9	36.7	30.5	29.0
14.1	22.9	33.1	24.4	44.5	30.4	29.5
R2-	32.3	30.6	24.8	44.6	30.4	29.6

<u>Solvent</u>	<u>Sadtler Ref.</u>	<u>Book Number</u>
CDCl ₃	429C	—
CDCl ₃	4144C	13
CDCl ₃	9316C	14

HEXANE



SOURCE OF SAMPLE Phillips Petroleum Co.
Bartlesville, Oklahoma

CHEMICAL FORMULA C_6H_{14}
 MOLECULAR WT. 86.18
 PROTON NMR NO. 3431 M
 MELTING POINT -95°C
 BOILING POINT 68.8°C

SOLUTION CONC. 50% v/v
 SOLVENT CDCl_3
 REFERENCE TMS
 TRANSIENTS 1000
 TIME 20 minutes
 SWEEP OFFSET -

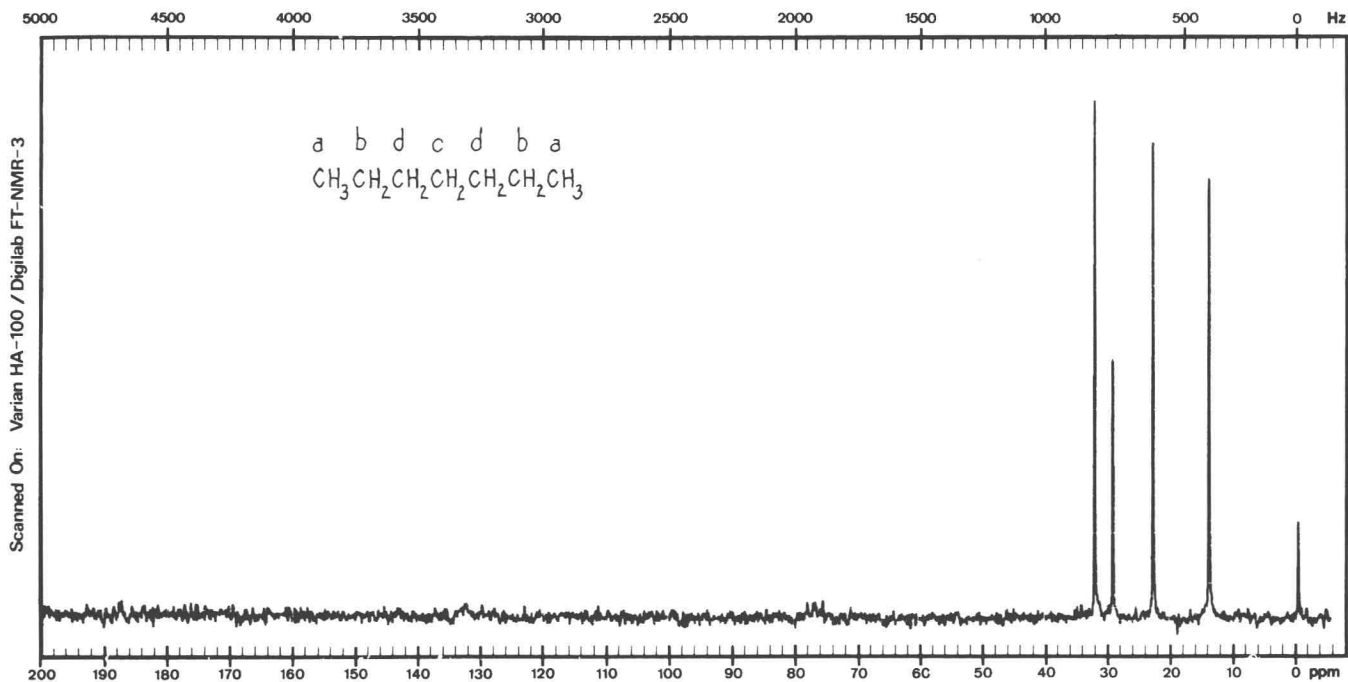
ASSIGNMENTS

A 14.2
 B 23.0
 C 32.1
 D _____
 E _____
 F _____
 G _____
 H _____
 I _____
 J _____
 K _____
 L _____
 M _____

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ALKANES

HEPTANE



SOURCE OF SAMPLE MCB Manufacturing Chemists
Norwood, Ohio

CHEMICAL FORMULA C_7H_{16}
 MOLECULAR WT. 100.21
 PROTON NMR NO. 679 M
 MELTING POINT -91°C
 BOILING POINT $98-99^\circ\text{C}$

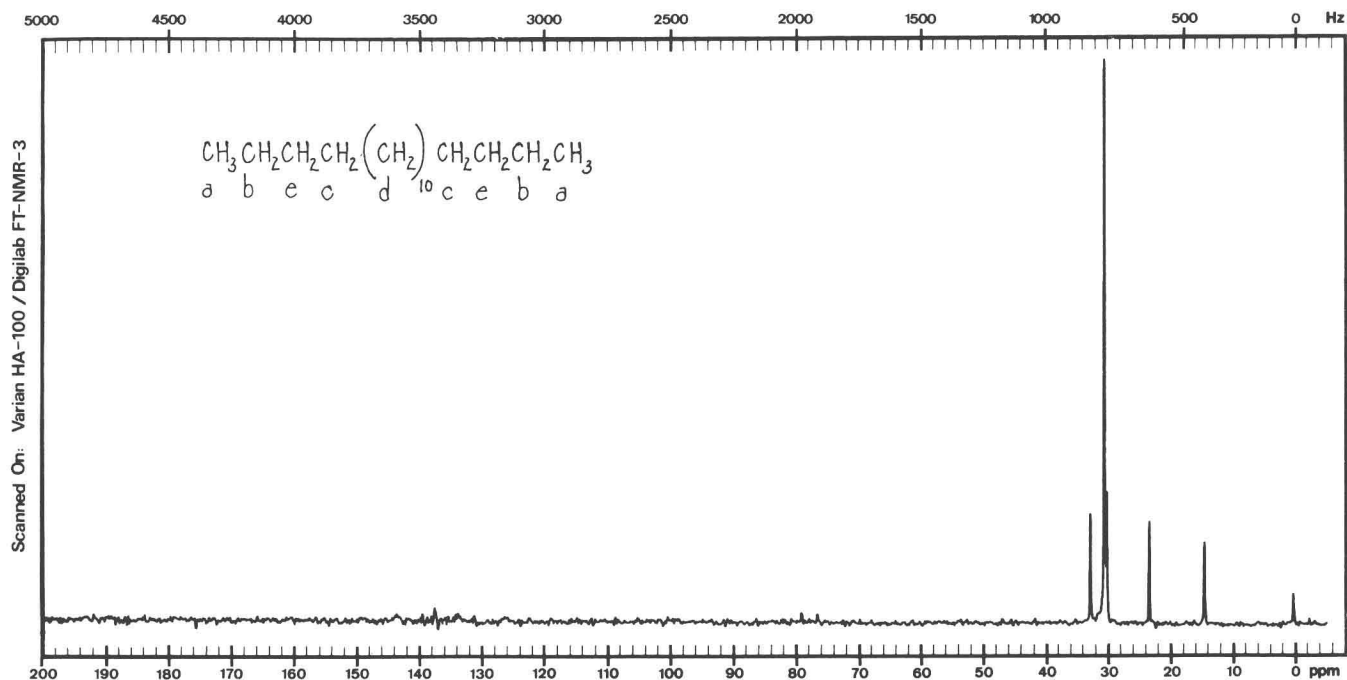
SOLUTION CONC. 50% v/v
 SOLVENT CDCl_3
 REFERENCE TMS
 TRANSIENTS 700
 TIME 14 minutes
 SWEEP OFFSET -

ASSIGNMENTS

A 14.1
 B 23.1
 C 29.5
 D 32.4
 E _____
 F _____
 G _____
 H _____
 I _____
 J _____
 K _____
 L _____
 M _____

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OCTADECANE



SOURCE OF SAMPLE MCB Manufacturing Chemists
Norwood, Ohio

CHEMICAL FORMULA $\text{C}_{18}\text{H}_{38}$
MOLECULAR WT. 254.50
PROTON NMR NO. 5310 M
MELTING POINT 29-30°C
BOILING POINT 317°C

SOLUTION CONC. 50% v/v
SOLVENT CDCl_3
REFERENCE TMS
TRANSIENTS 400
TIME 8 minutes
SWEEP OFFSET -

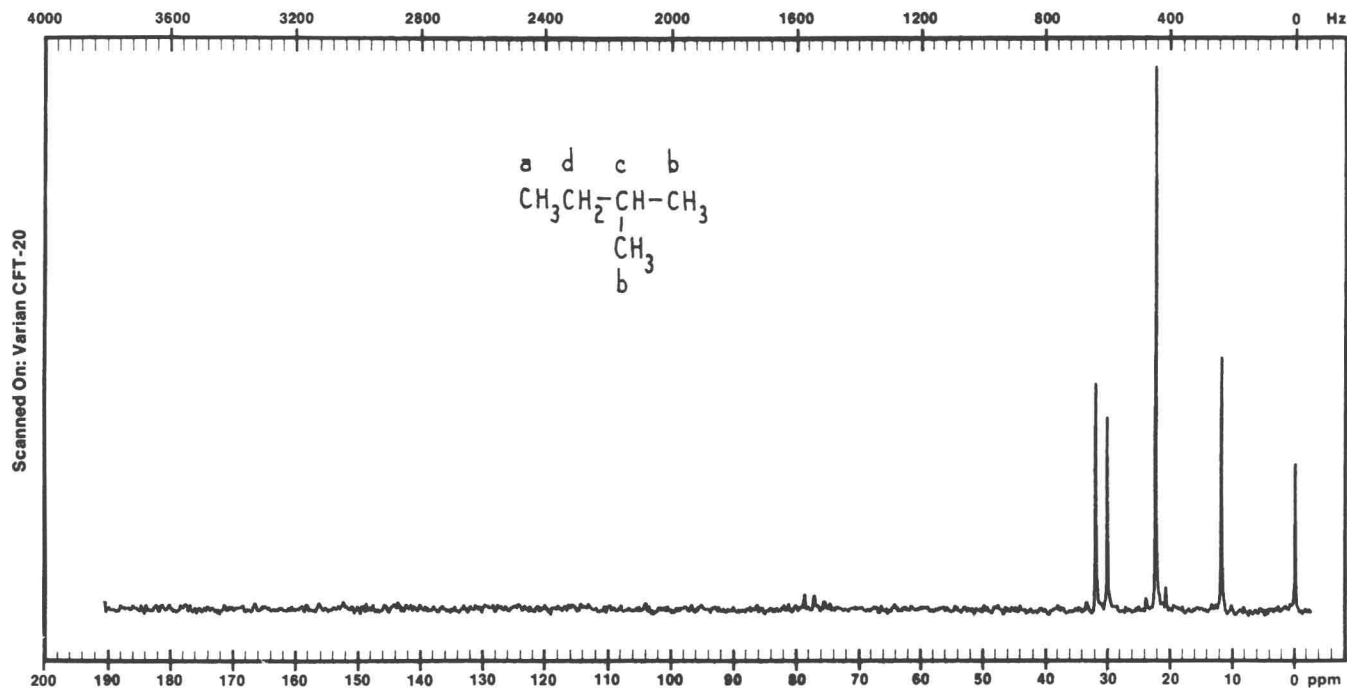
ASSIGNMENTS

A 14.2
B 22.9
C 29.6
D 29.9
E 32.2
F _____
G _____
H _____
I _____
J _____
K _____
L _____
M _____

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ALKANES

2-METHYLBUTANE



SOURCE OF SAMPLE MCB Manufacturing Chemists
Norwood, Ohio

CHEMICAL FORMULA C_5H_{12}

MOLECULAR WT. 72.15

PROTON NMR NO. 3416M

BOILING POINT 27.8°C

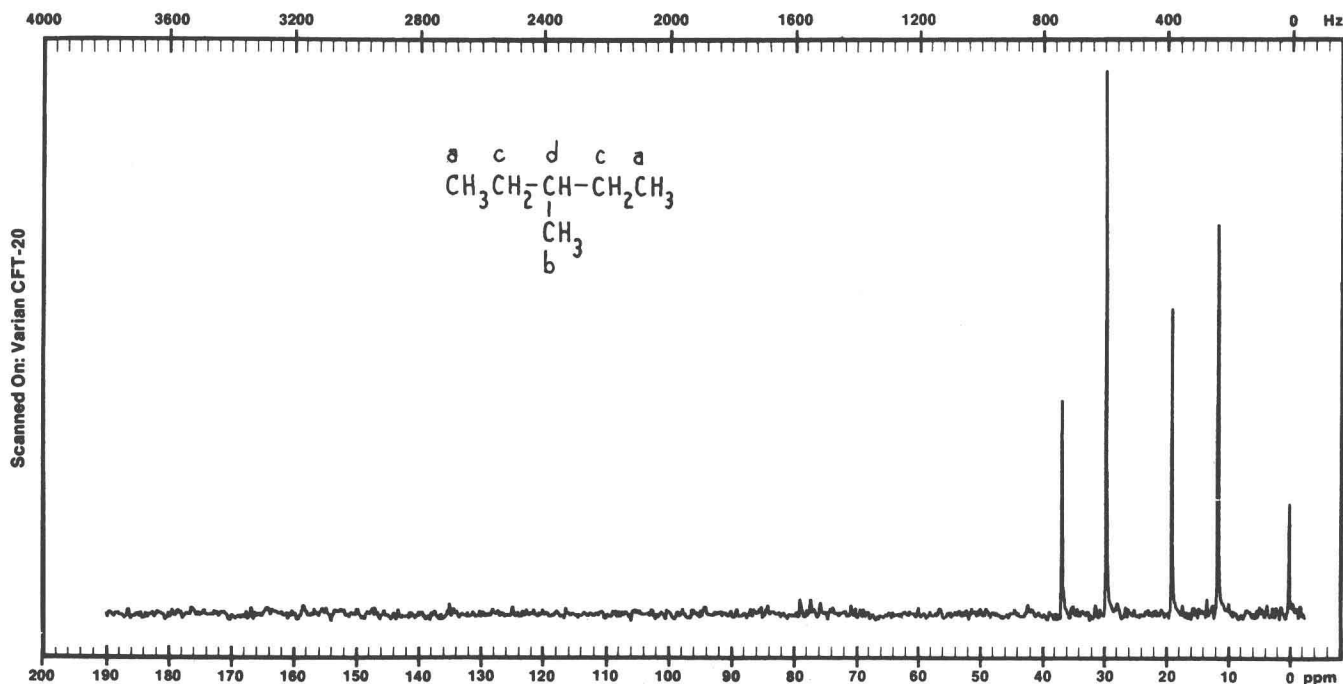
SOLVENT CDCl_3
REFERENCE TMS
SWEEP OFFSET -

ASSIGNMENTS

A 11.8
 B 22.3
 C 30.1
 D 32.0
 E _____
 F _____
 G _____
 H _____
 I _____
 J _____
 K _____
 L _____
 M _____

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3-METHYLPENTANE



SOURCE OF SAMPLE MCB Manufacturing Chemists
Norwood, Ohio

CHEMICAL FORMULA C_6H_{14}

MOLECULAR WT. 86.18

PROTON NMR NO. 3412M

BOILING POINT $63.3^\circ\text{C}(\text{lit.})$

SOLVENT
REFERENCE
SWEEP OFFSET

CDCl_3
TMS
-

ASSIGNMENTS

A 11.6
B 18.9
C 29.5
D 36.6
E _____
F _____
G _____
H _____
I _____
J _____
K _____
L _____
M _____

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