Handbook of Proton-NMR Spectra and Data

Volume 1

Edited by

Asahi Research Center

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Edited by
Asahi Research Center Co., Ltd.
Tokyo, Japan

Supervised by
Shin-ichi Sasaki
Toyohashi University of Technology
Aichi, Japan

1985

Academic Press, Inc.
(Harcourt Brace Jovanovich, Publishers)
Tokyo Orlando San Diego New York
London Toronto Montreal Sydney

ACADEMIC PRESS JAPAN, INC.
Hokoku Bldg. 3-11-13, Iidabashi, Chiyoda-ku, Tokyo 102

United States Edition published by ACADEMIC PRESS, INC.
Orlando, Florida 32887

United Kingdom Edition published by ACADEMIC PRESS, INC. (LONDON) LTD.,
24/28 Oval Road, London NW1 7DX

ISBN: 0-12-064501-7
Library of Congress Catalog Card Number: 85-61909

PRINTED IN JAPAN

85 86 87 88 9 8 7 6 5 4 3 2

Foreword

Professor Sasaki's efforts have resulted in an outstanding work. Proton-NMR has been of the greatest importance in scientific technology and continues to be a sophisticated means of analysis. The information it provides is indispensable for molecular structure analysis. Those engaged in chemical research must always start by measuring the NMR spectrum of the compound they are working with. But measuring alone is not sufficient. The researcher must have available various handbooks containing other data to assist him with the interpretation of molecular structure. To be of use, such data handbooks must include charts and data prepared by expert researchers working with reliable samples measured by advanced equipment; and a great many of these charts and data must be gathered as well. In other words, it is necessary to expend a great deal of time, trouble, and, most of all, determination, to assemble the wealth of data required. Thus, though the need for such a collection and its usefulness are well understood by all, few are willing to undertake the task and it has rarely been attempted—until now.

The present data book is a triumph over all these difficulties. I congratulate Professor Sasaki on his outstanding achievement and plan to make great use of it myself, as well as recommend it to others.

Shizuo Fujiwara
Professor of Chemistry, Faculty of Science, Chiba University;
Professor Emeritus, The University of Tokyo

Preface

With the recent shift to fine or specialty chemicals from commodities and the strong demand by high technologies for new materials, more complex organic compounds are synthesized, extracted, and purified. In order to analyze the molecular structure of these organic compounds quickly and precisely, a sophisticated method of instrumental analysis is absolutely necessary.

Because NMR permits the analysis of the fine structure of organic compounds, it is increasingly employed in the fields of research and development. It is, however, difficult to fully analyze NMR spectra because of the high level of knowledge and skill that this requires. Especially of late, as NMR has come to be employed beyond the chemical and pharmaceutical industries in such industries as electronics, machinery, and engineering, providing systems to support the molecular structure analysis of compounds by researchers has attained greater importance.

^{13}C-NMR provides a spectrum that is relatively simple and easy to analyze, and data books and databases have been developed in many countries such as the United States and Germany. The spectrum provided by ^{1}H-NMR is, however, relatively complex, and a spectrometer with higher resolution power is required. In addition, it is necessary to make all spectra measurements under constant conditions. Finally, a very knowledgeable and experienced specialist is needed to carry out this exacting work with care. As a result, there is as yet no completely satisfactory data collection for ^{1}H-NMR spectral analysis.

Taking all of these facts into consideration, we have carried out all spectra measurements ourselves and had them analyzed by fully qualified specialists. Collecting samples provided by research facilities affiliated with universities and by private companies, we have endeavour to encompass a rich variety of the newest organic compounds, to meet the needs of the handbook's users.

The spectral analysis system has been presented for public use in several different forms, but in response to researchers' strong requests to be able to look directly at spectral charts, we have designed our handbook accordingly.

Acknowledgments

This data handbook grew out of the spectral interpretation system that has been developed jointly by Toyohashi University of Technology and Asahi Research Center Co., Ltd. The Research Center for Chemometrics at Toyohashi University of Technology cooperated with Asahi Research Center in gathering organic samples, measuring spectra, and assignment. At present, more than ten thousand data have been accumulated, and it is only a matter of time before all become available for public use. We have selected and edited four thousand of those data to create the first five volumes of our data handbook.

We took great pains to ensure the quality and proper assignment of the spectra and the accuracy of the additional data, but hope that those who use the handbook will inform us of any oversights or errors so that we may correct them.

General reagents were mostly provided by Tokyo Kasei Kogyo Co., Ltd., and Kanto Chemical Co., Inc., whose cooperation in this endeavour was much appreciated. Many active researchers all over Japan also contributed valuable samples of the compounds they are working with. To all who offered samples go our deepest thanks.

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A User's Guide

This data handbook has been planned as a part of projected open-ended series, with publication of additional data books scheduled upon completion of further data compilation. The handbook consists of proton-NMR spectra and data for 4,000 organic compounds, divided into five volumes with 800 entries each. The handbook is divided into data sections and index sections.

1. Proton-NMR Spectra and Data Sections

All data entries are in the form:

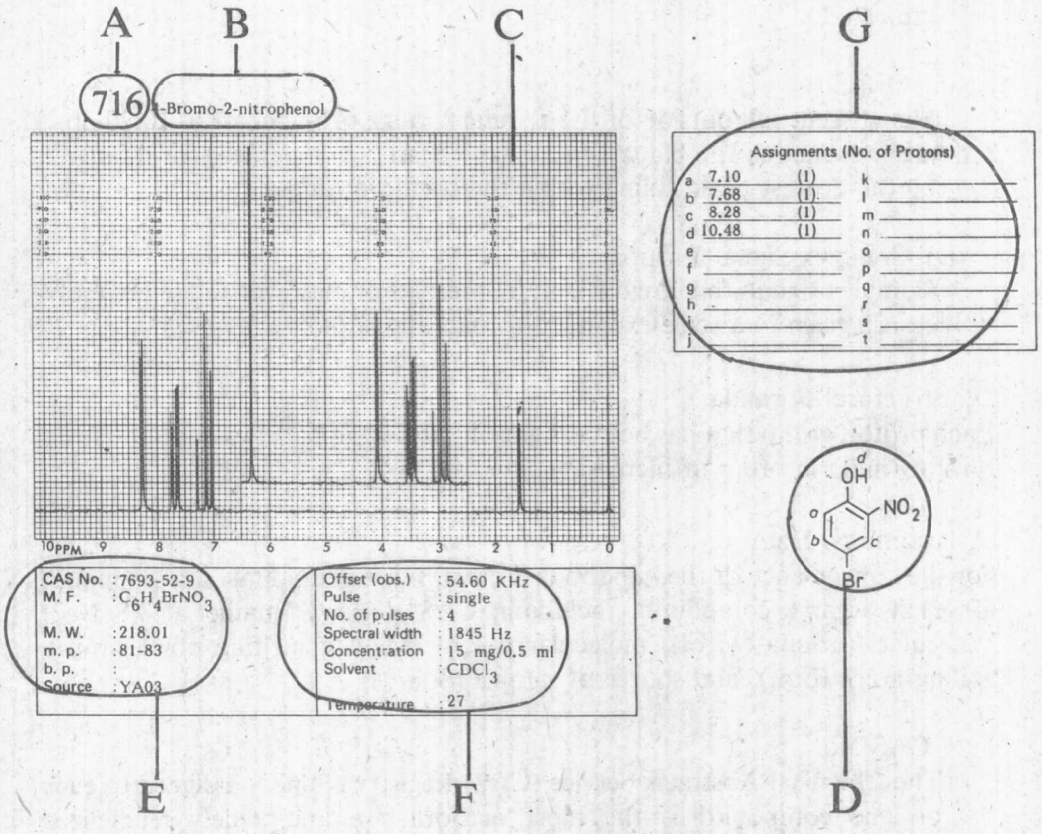

Figure 1. Illustration of Spectral Data

A. Spectrum Number

The organic compounds for which spectral data are provided are arranged in order of molecular complexity, from simpler to more complex. Each entry is assigned a number in sequence which serves as a key for easy indexing and quick reference.

B. Chemical Name

In general, all chemical names are in accord with the IUPAC nomenclature system. There are, however, some compounds that are more frequently referred to by trivial names, such as vanillin. In these cases, the trivial name is used.

C. Spectrum

(i) Units

For easy recognition of peak positions of signals, the smallest unit of the spectrum chart is 0.1 ppm (9 Hz).

(ii) Impurities

Signals resulting from a trace amount of impurities in the sample are indicated by the letter "i" over the signal in question. Signals resulting from impurities in the solvent, however, such as $CHCl_3$ in $CDCl_3$, are not indicated.

(iii) Offset

Signals that fall outside of the standard range of the chart (0-10.20 ppm) are indicated in the blank space of the chart accompanied, for reference, by the nearest peak falling within the standard range.

(iv) Complex Signal Groups

Complex signals that are difficult to interpret or may even fail to be resolved are given in a scale-expanded format above the original signal.

D. Structural Formula

Each proton group that has been assigned is labeled alphabetically on the structural formula in order of increasing chemical shift.

E. Additional Data

For the convenience of the handbook's users, some additional data is supplied for each organic compound, including: CAS Registry Number (CAS No.), molecular formula (M.F.), molecular weight (M.W.), melting point (m.p.), boiling point (b.p.), and source of sample (Source).

(i) CAS No.

The Chemical Abstracts Service (CAS) Registry Number assigned to each organic compound is the most authoritative and widely recognized chemical identification number. As a result, it is extremely helpful as a link

to information available in many other database systems such as CAS-ONLINE and CIS, among others.

(ii) Molecular Formula

Molecular formulas are arranged according to the Hill system, that is, C before H, with all other elements in alphabetical order.

(iii) Molecular Weight

Average molecular weights derived from average atomic weights are given.

(iv) Melting and Boiling Points

Both values are recorded in Celsius, based on the literature or data recorded by sample suppliers. In the case of compounds that decompose, the decomposition point is given, as, for example, 250 dec.

(v) Source of Sample

Sample suppliers are recorded in a four-letter code. Full identification of suppliers is provided in Chart 5.

F. Spectrum Measurement

(i) Spectrometer

The spectrometer used for all measurements is an FX-90Q manufactured by JEOL Ltd. This is a modern Pulse Fourier Transform spectrometer. The 90 MHz spectrometer is the most widely used spectrometer at present.

(ii) Specifications

The specifications for the spectrometer are as follows:

- Magnetic field — 21100 gauss
- Observation frequency — 89.55-89.65 MHz
- NMR lock — D2 internal lock
- Insert coil — 5 mm diameter
- Resolution — $^1H \leqq 0.2$ Hz
- Pulse mode — Single
- Accumulation times — Four (average)
- Data points — 16 K

(iii) Measurement Conditions

Spectra measurements are carried out under constant conditions as much as possible. Measurement is carried out, as a rule, at 27°C. In most cases, the solvent used is $CDCl_3$; D_2O, DMSO-d_6, or polysol, a mixture of $CDCl_3$ and DMSO-d_6 which is used as a solvent for compounds that do not dissolve in $CDCl_3$. Tetramethylsilane (TMS) is employed as the internal standard except when the solvent is D_2O, in which case 3-(trimethylsilyl)propionic acid-d_4 sodium salt (TSP-d_4) is employed.

G. Assignment

Assignment is carried out in order of increasing chemical shift relative to TMS or TSP-d_4. Related proton groups are identified with letters of the alphabet for easy correlation.

Integration curves have been omitted from the spectra chart because of the problem of poor legibility. The number of assigned protons is recorded instead in parentheses following the chemical shift value.

Determination of the chemical shift value has been carried out by standard methods. In addition, digital output from the spectrometer has been referred to. For those multiplets for which first-order approximation is sufficient, the center of the multiplets has been regarded as the chemical shift. For those which clearly exhibit a second-order signal pattern, when all the signals constituting the multiplet can be positively identified, the first approximation or the center of the multiplet is regarded as the chemical shift.

Spin-spin coupled multiplets with complex overlapping are represented by the appropriate signal range, as, for example, 7.22-8.54.

When assignment is difficult because of similar chemical environments of proximate molecular structures or overlapping signals, the several alternative assignment values are each marked with an asterisk and a number which indicates that other asterisked values of the same number may be interchangeable.

When no appropriate signal is observable throughout the entire spectrum, the proton group is marked u.o. (unobserved). When the appropriate signal clearly overlaps with another signal and the chemical shift value is difficult to determine, the proton group is marked u.d. (undetermined). When the precise chemical shift value cannot be determined but an extremely close approximation is possible, the value is marked with the prefix ca. (circa).

2. Index Sections

Thorough, carefully prepared indexes are crucial tools for effective use of any data collection. Four types of exhaustive indexes accompany the present handbook, designed for quick and convenient cross checking, in a handy format that provides extremely useful combinations of data at a glance and greatly enhances the use of the entire handbook. The indexes and the data they contain are as follows:

Table 1

Index Name	First Column	Second Column	Third Column
Chemical Name Index	Chemical name	Spectrum No.	
Molecular Formula Index	Molecular formula	Chemical name	Spectrum No.
Substructure Index	Substructure	Chemical shift	Spectrum No.
Chemical Shift Index	Chemical shift	Substructure	Spectrum No.

A. Chemical Name Index

All chemical names are in alphabetical order. Numerals, Greek characters,

and codes indicating substitution positions (such as 1-, beta-, N-, etc.) and geometrical, stereochemical, and optical isomeric prefixes (such as cis-, endo-, levo-, etc.) are disregarded in alphabetization. Each name is followed by a spectrum number, as can be seen in the sample page of the Chemical Name Index (Chart 1).

B. Molecular Formula Index

When the desired organic compound cannot be found in the Chemical Name Index or its nomenclature is unclear, it becomes necessary to look for a compound by means of its molecular formula. This is just the case for which the Molecular Formula Index was designed. Molecular formulas are listed following the Hill system, in order of complexity. When several compounds have the same molecular formula, the different compounds are listed in alphabetical order, as can be seen in the sample page of the Molecular Formula Index (Chart 2). The spectrum number is also provided for easy cross reference to the data handbook.

C. Substructure Index

Determining what sorts of proton correspond to the various signals within a spectrum, investigating their chemical environments, and suggesting models for their structure are all very important parts of spectral analysis.

A unique notation system for representing substructure has been developed in the Substructure Index to allow easy correlation of the chemical environments of protons and chemical shift, and at the same time permit fast consideration of a wide variety of model structures.

In the substructure notation of the index, the proton group which is assigned as the TARGET is grouped with its neighbors (e.g. α position) and next nearest neighbors (e.g. ß position). The TARGET occupies the head position of the substructure notation, as can be seen in Fig. 2. It is followed by the neighboring atoms, given outside parentheses; the next-nearest atoms are written inside parentheses.

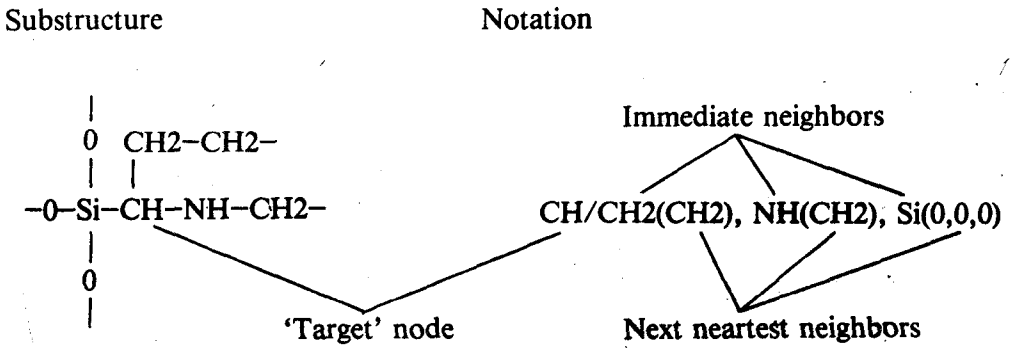

Figure 2. Substructure Notation

All non-identical substructures relating to a particular TARGET are cited in the index. In order to simplify the substructure notation, single bonds have not been represented. Code for other atomic groups is found in Chart 3-1, as is their order of priority. Chart 3-2 shows a sample page of the Substructure Index. For the user's convenience, chemical shift value and spectrum number are also provided for each entry.

D. Chemical Shift Index

Entries on the Chemical Shift Index are arranged in order of increasing delta value (ppm). For easy correlation of chemical shift with substructure, substructure notations are listed for each entry as well. Chart 4 shows a sample page of the Chemical Shift Index.

Chart 1. The Chemical Name Index

Chart 2. The Molecular Formula Index

Chart 3-1. The Code Table of Substructure Notation

Priority	Code	Substructure	Priority	Code	Substructure
1	CH3	$-CH_3$	25	=N=	=N=
2	CH2	$-CH_2-$	26	N〔*	aromatic nitrogen
3	CH	-CH<	27	NO2	$-NO_2$
4	C	>C<	28	#N	≡N
5	CH2=	$=CH_2$	29	OH	-OH
6	CH=	=CH-	30	O	-O-
7	CH=〔E〕	=CH- a〕	31	=O	=O
8	CH=〔Z〕	=CH- b〕	32	SH	-SH
9	C=	=C<	33	S	-S-
10	=C=	=C=	34	=S	=S or =S<
11	#CH	≡CH			
12	C#	≡C-	35	SO2	$-SO_2$
13	AH	c〕	36	P	-P<
14	A	d〕	37	PH=	=PH
15	TPL	e〕	38	P=	-P= or >P=
16	CHO	-CHO	39	F	-F
17	C=O	>C=O	40	CL	-Cl
18	=C=O	=C=O	41	BR	-Br
19	$NH3^+$	ammonium cation	42	I	-I
20	NH2	$-NH_2$	43	AS	>As-
21	NH	>NH	44	AS=	=As-
22	N	>N-	45	SI	>Si<
23	=NH	=NH	46	+	cation
24	N=	-N=	47	-	anion
			48	·	radical
			49	/	chelation
			50 f〕	X	other atoms

a) Entgegen b) Zusammen c) Aromatic carbon with proton
d) Aromatic carbon without proton e) -C(OH)-C(O)- in troponoid
f) Other element symbols are listed in alphabetical order.