STRUCTURAL ANALYSIS OF ORGANIC COMPOUNDS BY SPECTROSCOPIC METHODS

Structural Analysis of Organic Compounds by Spectroscopic Methods

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MACDONALD : LONDON
AMERICAN ELSEVIER : NEW YORK

This English edition is a translation of
a specially revised version of
Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden
First published in 1967 by
Akademische Verlagsgesellschaft
Frankfurt am Main

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English edition published under licence by
Macdonald & Co. (Publishers) Ltd
49/50 Poland Street, London W.1

English edition © 1971 Macdonald & Co. (Publishers) Ltd

Published in United States by
American Elsevier Publishing Company, Inc.
52 Vanderbilt Avenue, New York, New York 10017

Translated by Transcripta Services

British SBN 356 03052 0
American SBN 444 19605 6
Library of Congress Catalog Card Number 74-150948

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Printed and bound in Great Britain by
Hazell Watson and Viney Ltd, Aylesbury, Bucks

Foreword

Instrumental methods, especially infrared, nuclear resonance, mass and electronic spectroscopy, have in recent years become very important for the elucidation of the structure of organic compounds. The number of textbooks and particularly of monographs has increased correspondingly to an alarming degree. The especial effectiveness of the combined use of these four methods for the structural elucidation of organic compounds was first impressively shown in 1963 by R. M. Silverstein and G. C. Bassler in 'Spectrometric Identification of Organic Compounds'. Today this combination is already being taught systematically in various well-known colleges. Experience gained from courses and seminars in the organic chemistry laboratory, Eidgenössiche Technische Hochschule, Zürich, was used in the compilation of the tables given in this book. No claim to comprehensiveness is made; instead data have been selected which by experience have been found sufficient for the interpretation of the spectra of relatively simple compounds. The tables are intended primarily for those who wish to make use of the advances in instrumental analysis without having an expert knowledge of the various spectroscopic methods. Consequently only a basic knowledge, such as today is found in the basic training of an organic chemist, is assumed. There are doubtless omissions in the tables and we should be grateful to have these brought to our attention and also for suggestions for improvements.

We should like to take this opportunity to thank all those who have been in any way involved in the production of this book. We especially thank Dr. C. Pascual, Priv.-Doz. Dr. J. Seibl and J. A. Völlmin for their collaboration in the preparation of tables in their own fields. Likewise we thank the technicians of our instrumental analytical department for recording the spectra.

W. Simon
Zürich, July 1966 J. T. Clerc

Editor's Foreword

The book in this Series *Applications of Spectroscopy to Organic Chemistry* by Brand and Eglinton provides for honours students a review of spectroscopic principles and, by means of examples and problems, shows the relationships between structure and spectra. The successful application of spectroscopic methods depends on experience and practice and this volume by Simon and Clerc is regarded as complementary to the earlier text, in providing a large number of additional examples and problems. It is also likely to be a valuable reference book at research level.

M. F. Grundon

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Introduction

In the following tables abbreviations have been avoided as far as possible. Long explanations are therefore unnecessary and only the following general notes are given.

IR: Infrared spectroscopy

Data given: wave number $\bar{\nu}$ (cm^{-1}) of absorption maxima of solutions in solvents of low polarity such as CCl_4, CS_2, $CHCl_3$ etc. The following abbreviations are used for the assignment of individual absorption bands and for intensity data:

s.	strong
m.	medium
w.	weak
v.	variable
st.	stretching vibration
skel.	skeletal vibration
def.	deformation vibration
as.	asymmetric
sy.	symmetric

UV: Spectroscopy in ultraviolet and visible regions (electronic spectroscopy)

Data given: wavelength λ_{max} (nm) of absorption maxima of ethanolic solutions; decadic logarithm log ε of molar extinction coefficient ε at the corresponding wavelength.

NMR: Proton resonance spectroscopy

Data given: chemical shift δ (ppm) based on tetramethylsilane (TMS) as internal reference in solutions in $CDCl_3$ or CCl_4: Coupling constants J (Hz).

MS: Mass spectroscopy

Data given: mass to charge ratio, m/e, of corresponding fragments. The molecular ion is represented by M.

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Table 1

Type of compound: **C—C alkane**

	Position	Assignment	Notes
IR	2960...2850 cm^{-1} s.	CH st.	See also: H–  : ~3050 cm^{-1} H—C—Hal : ~3010 cm^{-1} CH_3O— : 2830...2815 cm^{-1} CH_3N— : ~2800 cm^{-1} —O—CH_2—O— : ~2780 cm^{-1} H—C(=O)— : 2880...2650 cm^{-1} (usually two bands) Also in same region: =CH— st.; ArH st.; OH assoc. st.
	~1460 cm^{-1} m.	CH_3 def. as. CH_2 def.	'Activated' as with CH_2 groups adjacent to C=C or Ar at 1440...1400 cm^{-1}. → Table 21.
	~1380 cm^{-1} m.	CH_3 def. sy.	Doublet for gem. methyl groups → Table 23. Missing for compounds with no CH_3 groups. In methyl ketones, acetates at 1360...1340 cm^{-1}.
	1350...1100 cm^{-1} v.	C—C st. skel. CH def.	No practical importance except for gem. CH_3 groups → Table 23.
	~720 cm^{-1} v.	skel.	Rocking of —CH_2—. Present for —$(CH_2)_{\bar{n}\geq 4}$. For $n<4$ at higher frequencies (up to 800 cm^{-1})—and less intense, often invisible; for cyclohexanes at ~890 cm^{-1}. See also: —O—$(CH_2)_{\bar{n}\geq 4}$: ~740 cm^{-1}. Also in same region: =CH def. (out-of-plane); ArH def. (out-of-plane); NH_2 def. (out-of-plane); NO def.; CS st.; SO st.; PC st.; CCl st.; ring def.; —$OC(CH_3)_3$ skel.

UV-, NMR- and MS- data continued on the next page

Table 1 (cont.)

	Position	Assignment	Notes
UV	none above 210 nm		For saturated hydrocarbons.
NMR	0.8...1.2 ppm	$C-CH_3$	Characteristic pseudotriplet for $—CH_2—CH_2—CH_3$.
	1.1...1.8 ppm	$\left\{\begin{array}{l} C-CH_2-C \\ C-CH-C \\ \quad\quad\vert \\ \quad\quad C \end{array}\right\}$	Estimation of chemical shift → Table 41. Alicyclics with at least 6-membered rings give usually a broad, unstructured signal.
			See also: H—  : **−0.3...0.8 ppm** J_{CH-CH} : **6...7 Hz** if freely rotatable; → Table 44.
MS		Molecular ion	*n-Alkanes:* weak *Isoalkanes:* very weak } $\frac{m}{e} = 14\,n + 2$. *Monocycloalkanes:* moderately intense $\frac{m}{e} = 14\,n$.
		Fragments	*n-Alkanes:* $\frac{m}{e}$ = 29, 43, 57, 71, 85...$14n + 1$; continuous variation in intensity; max. at $\frac{m}{e}$ = 43 or 57; min. at $\frac{m}{e} = M-15$.
			Isoalkanes: $\frac{m}{e}$ = 29, 43, 57, 71, 85...$14n + 1$; irregular variation in intensity; relative max. from fragmentation at branching position. The charge predominantly stays on the more highly branched fragment. Same order of peaks also with aliphatic carbonyl compounds, but these have rearrangement peaks at $\frac{m}{e} = 14n + 2$.

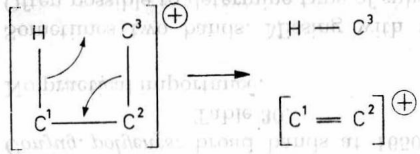
Monocycloalkanes: $\frac{m}{e} = 27, 41, 55, 69, 83 \ldots 14n-1$; relative max. from fragmentation of bond to ring.
Same peak order also with alkenes and alcohols.

Polycycloalkanes: $\frac{m}{e} = 41, 55, 67, 81, 93, 95, 107;$
Same order of peaks also with polyolefines.

Rearrangements

n-Alkanes: none

Isoalkanes: frequently 1→3 rearrangement, $\frac{m}{e} = 14n$:



Rearrangement occurs particularly if:
1. C^2: quat. > tert. > sec.
2. C^3: quat. > tert. > sec.
3. C^1: tert. > sec. > prim.

Monocycloalkanes: frequently 1 → 3 rearrangement, $\frac{m}{e} = 14n-2$.

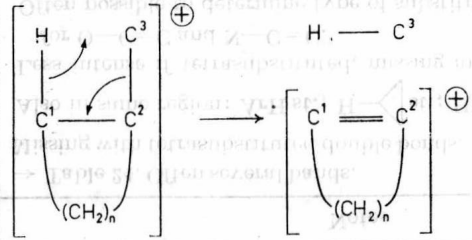


Table 2

Type of compound: **C=C alkene**

	Position	Assignment	Notes
IR	3100...2975 cm^{-1} m.	=CH st.	→ Table 24. Often several bands. Missing with tetrasubstituted double bonds. Also in same region: ArH st.; H—⟨ st.; HCHal st.; OH assoz. st.
	1690...1640 cm^{-1} v.	C=C st.	Less intense if tetrasubstituted, missing at higher symmetry; intense for O—C=C and N—C=C. Often possible to determine type of substitution → Table 24. Also in same region: C=O conjug. st.; NH def. (in-plane); C=N st. NO st. *Enols:* C=C st.: ~1605 cm^{-1}; C=O st.: ~1640 cm^{-1}; → Table 8. *Conjug. dienes:* 2 bands at ~1650 cm^{-1} and ~1600 cm^{-1}; → Table 29; → Table 30. *Conjug. polyenes:* broad bands at 1650...1580 cm^{-1}; → Table 29; → Table 30.
	1420...1290 cm^{-1} w.	=CH def. (in-plane)	No practical importance.
	990... 675 cm^{-1} s.	=CH def. (out-of-plane)	Sometimes two bands. Missing with tetrasubstituted double bonds. Often possible to determine type of substitution → Table 24. Also in same region; $-(CH_2)_{n>4}$ skel.; ArH def. (out-of-plane); CH def. (out-of-plane), OH assoz. def. (out-of-plane); C—C skel.; NH_2 def. (out-of-plane); NO def.; CS st.; SO st.; PC st.; CCl st.; Ring def.; $-OC(CH_3)_3$ skel.; C(=O)—H def. (out-of-plane). See also: CH_2—C=C def.: 1445...1430 cm^{-1}.
UV	none above 210 nm		For isolated double bonds; if highly substituted often end absorption >210 nm. *Conjug. polyenes:* >220 nm (log ε = 4...5) $\pi \rightarrow \pi^*$; → Table 30. Estimation of λ_{max}: → Table 29.

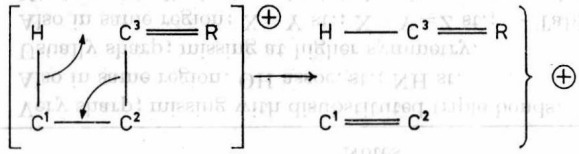
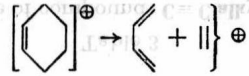
NMR	4.5...8.0 ppm	C=C–H	Estimation of chemical shift: → Table 42. $J_{C-C\langle H \atop H}$: **0...3,5 Hz** $J_{H\ \ H \atop C-C\langle H}$: **5...14 Hz** $J_{C-C\langle H}$: **12...18 Hz** **$J_{CH-C-CH}$: 0...3 Hz** The coupling constants are dependent on electronegativity of the substituents at the double bond; → Table 44. See also: CH_3—C=C: 1.6...1.8 ppm; CH_2—C=C: 1.7...2.4 ppm.
MS		Molecular ion	Moderately intense $\frac{m}{e} = 14n$.
		Fragments	$\frac{m}{e}$ **= 27, 41, 55, 69, 83,... 14n − 1;** in many cases base peak formed by fragmentation between α- and β-position to double bond. Care: double bond readily migrates! Same order of peaks for monocycloalkanes and alcohols.
		Rearrangements	Frequently 1 → 3 rearrangement, $\frac{m}{e} = 14n - 2$.  Formation of preferentially stabilised ions. In cyclohexenes often also retro-Diels-Alder reaction:  Formation of preferentially stabilised ions.

Table 3

Type of compound: **C≡C alkyne**

	Position	Assignment	Notes
IR	~3300 cm^{-1} w.	≡CH st.	Very sharp; missing with disubstituted triple bonds. Also in same region: OH assoc. st.; NH st.
	2260...2100 cm^{-1} w.	C≡C st.	Usually sharp; missing at higher symmetry. Also in same region: X≡Y st.; X=Y=Z st.; → Table 22.
	700...600 cm^{-1}	≡CH def. (out-of-plane)	Missing with disubstituted triple bonds; no practical value.
			See also: CH_2—C≡C def.: 1445...1430 cm^{-1}.
UV	>210 nm end absorption		Often several weak bands < 240 nm (log ε = 1...2)
NMR	2.0...3.2 ppm	C≡C—H	$J_{CH-C\equiv CH}$: 2...3 Hz See also: CH_3—C≡C: ~1.8 ppm CH_2—C≡C: ~2.0 ppm
MS		Molecular ion Fragments Rearrangements	Weak; usually missing with 1-alkynes. Fluctuating between aromatic and alkane types

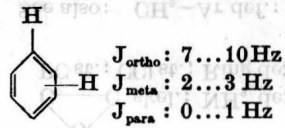
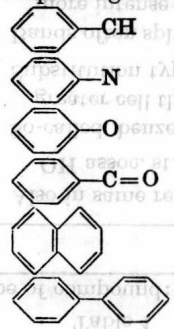
Table 4

Type of compound: **aromatic**

	Position	Assignment	Notes
IR	3080...3030 cm^{-1} v.	ArH st.	Also in same region: =CH st.; H—  st.; HCHal st.; OH assoc. st.
	2000...1660 cm^{-1} w.	Combinations and overtones	So-called benzene finger. Only clear at higher concentration and/or greater cell thicknesses. Substitution type often determinable; → Table 25.
	1625...1575 cm^{-1} v.	skel.	Bands often split. Bands at ~1500 cm^{-1} sometimes missing, but usually more intense than bands at ~1600 cm^{-1}.
	1525...1475 cm^{-1} v.	skel.	Also in same region: C=C conjug. st.
	1460...1440 cm^{-1} v.	skel.	
	1225...950 cm^{-1} w.	ArH def. (in-plane)	Often several bands; intense in presence of polar substituents, no practical importance.
	900...735 cm^{-1} m. s.	ArH def. (out-of-plane), skel.	1 to 3 bands. Substitution type often determinable; → Table 25. Also in same region; $-(CH_2)_{n>4}$ skel.; =CH def. (out-of-plane);  skel.: NH_2 def. (out-of-plane); NO def.; CS st.; SO st.; PC st.; CCl st.; Ring def.; $-OC(CH_3)_3$ skel.; H—  def. (out-of-plane).
			See also: CH_2—Ar def.: 1445...1430 cm^{-1}.

UV-, NMR- and MS- data continued on the next page

Table 4 (cont.)

	Position	Assignment	Notes
UV	**205...260 nm** (log $\varepsilon = \sim 4$) **260...300 nm** (log ε = **2.5...3.5**)		→ Table 34, → Table 35. → Table 36. Conjugation raises ε and shifts λ_{max} to higher wavelengths.
NMR	6.5...8.5 ppm	**ArH**	Estimation of chemical shift: → Table 42.  See also: CH_3—Ar: 2.2...2.5 ppm singlet C—CH_2—Ar: 2.3...2.8 ppm
MS		Molecular ion Fragments	Very intense, often base peak. $\frac{m}{e}$ = 39, 50...53, 63...65, 75...78; higher substitution causes shift to lower values. Doubly charged ions frequent. Depending on substitution the following intense peaks appear: 

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