

2 Carbon-13 NMR of aromatic compounds

2.1 Introduction for 2

The ^{13}C isotope of carbon possesses a spin quantum number of $\frac{1}{2}$, a feature that places it among the most suitable nuclei for routine NMR measurements. However, the sensitivity of the ^{13}C resonance is approx. 6000 times smaller than ^1H because of its lower natural abundance and magnetogyric ratio. The introduction of Pulse-Fourier-Transform (PFT) techniques and the commercial production of spectrometers with superconducting helium-cooled magnets and computers substantially overcame this problem and brought about rapid development of ^{13}C -NMR spectroscopy in the early 1980s. Until nowadays many one- and two-dimensional multipulse techniques have been developed for recording and assigning the ^{13}C -NMR spectra. Along with ^1H spectra they have become the most important characteristic of synthetic and naturally occurring organic compounds.

The range of the ^{13}C chemical shifts is normally 0-220 ppm, which is an advantage over the ^1H -NMR spectra exhibiting signals at a much lower range (about 15 ppm). The routine ^{13}C -NMR spectra are measured under conditions of decoupling from the carbon-proton interactions, which makes them appearing as usually not overlapping singlet signals. In this way they are lacking information about the coupling constants so that additional techniques are needed for their measurement. That is why coupling constants are not so popular in ^{13}C -NMR spectroscopy. Most significant are the so-called direct coupling constants i.e. between directly bonded nuclei (scalar coupling *via* one bond). Because of technical reasons long-range constants are not so easy to measure accurately.

^{13}C chemical shifts are less sensitive to anisotropic and solvent effects than the ^1H chemical shifts often allowing their relatively correct prediction and simple assignment and using them as fingerprint information. Stereochemistry and molecular dynamics can also be studied.

Deuterated solvents are commonly used for ^{13}C -NMR spectra, mostly deuterated chloroform (CDCl_3) with tetramethylsilane (TMS) as internal reference.

Referred below are some of the monographs giving detailed information about the theory, application and experimental aspects of ^{13}C -NMR spectroscopy.

2.2 References for 2.1

- Harris, R. K., Nuclear Magnetic Resonance Spectroscopy – A Physicochemical Review, Pitman, London (1983).
- Ernst, R. R., Bodenhausen, G., Wokaun, A.: Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Clarendon Press, Oxford (1987).
- Kalinowski, H-O., Berger, S., Braun, S.: Carbon-13 NMR Spectroscopy, Wiley, Chichester (1988).
- Wehrli, F. W., Marchand, A. P., Wehrli, S.: (2nd Ed.) Interpretation of Carbon-13 NMR Spectra, Wiley, Chichester (1988).
- Pretsch, E., Bühlmann, P., Affolter, C.: Structure Determination of Organic Compounds, Tables of Spectral Data, Springer, Berlin, Heidelberg (2000).

2.3 Organization of data

Aromatic compounds were studied very intensively by ^{13}C -NMR spectroscopy. Because of the vast amount of ^{13}C data existing in literature, natural aromatic compounds and heteroaromatics are not included. They can be found in separate volumes of this series. Solid phase spectra are also not reported.

The compounds are arranged by their gross formulae according to the Hill system, i.e. by the increasing number of C and H atoms followed by the other atoms in alphabetical order.

The numbering of the atoms is according to IUPAC system, but not in all cases. Sometimes for the sake of lucidity the nomenclature is not followed. The numbers of the carbon atoms are notified on the structures. For the monosubstituted compounds the C-atom bearing the substituent is always specified as number 1.

The data collection exists in two versions. Only chemical shifts data are reported in the printed version of this volume. In cases where coupling constants data are given in the CD-ROM version the substance is marked by an asterisk (*) in the column **Gross formula**.

The chemical shifts (in ppm) are reported with one decimal. The coupling constants nJ (in Hz), where n is the number of bonds between the coupling partners are given in the CD-ROM version with one decimal, except when the literature values are in integers. Coupling constants are reported as absolute values in order to avoid misassignments for constants where the signs have not been determined. However, in most cases only the absolute values are significant for chemical and stereochemical applications. The values of the chemical shifts and coupling constants marked with the same superscripts (^{a,b} etc.) could be interchanged according to the original literature. The note n.r. (not reported) means that no data are given in the original articles.

If there is more than one set of data found in literature, the data in CDCl_3 were preferred, or the data with the most signals assigned. As already mentioned in section 2.1 the C-13 data are in general not substantially dependent on the solvent. Nevertheless, in the accuracy of chemical shifts a tolerance up to 2-3 ppm should be allowed due to solvent effects, differences in referencing or instrumental reasons. That is why concentration data are not included in the tables. In most cases the ^{13}C spectra are measured at ambient temperature between 398 and 413 K. In the cases where the spectra were measured at higher or lower temperature it is indicated in the column **Solvent**.

Abbreviations

Ac	Acetone
Ar	Aryl
DAA	Dimethylacetamide
DBE	1,2-Dibromoethane
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
n.r.	not reported
Ph	Phenyl (C_6H_5)
TCE	1,2,2-Tetrachloroethane
THF	Tetrahydrofuran