Possibilities of multinuclear NMR in the chemistry of heteroorganic compounds*

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Results of multinuclear NMR studies of some heteroorganic compounds have been presented.

Key words: ^{15}N, ^{17}O, ^{51}V, ^{77}Se, ^{119}Sn NMR spectroscopy; heteroorganic compounds.

NMR spectra can be obtained for ~120 nuclei starting from a proton and reaching to the ^{235}U isotope.[1,2] Therefore from a chemist's point of view multinuclear magnetic resonance spectroscopy is one of the most useful methods. NMR spectroscopy does not suffer from the limitations of X-ray structure analysis, such as the availability of single crystals of good quality or absolute purity of the compounds under investigation. Moreover, the behavior of molecules in solution can differ remarkably from their characteristics in the crystalline state and, in these cases, NMR can be an especially useful method for the study of these dynamic phenomena.

Modern two-dimensional measuring techniques, such as homo- and heteronuclear chemical shift correlation spectroscopy based on polarization transfer through bonds (COSY)[3,4] and INADEQUATE[4] or on the Overhauser effect (NOESY),[5] provide especially useful information on intra- and intermolecular interactions.

The two-dimensional methods mentioned above have an enormous number of applications in ^{1}H and ^{13}C NMR spectroscopy. For isotopes characterized by a high natural abundance, such as ^{1}H, ^{11}B, ^{14}N, ^{23}Na, ^{27}Al, ^{31}P, ^{39}K, ^{45}Sc, ^{51}V, ^{55}Mn, ^{59}Co, ^{63}Cu, ^{69}Ga, ^{75}As, ^{79}Br, ^{81}Br, ^{89}Rb, ^{89}Y, ^{93}Nb, ^{99}Tc, ^{103}Rn, ^{107}Ag, ^{109}Ag, ^{115}In, ^{121}Sb, ^{123}Sb, ^{127}I, ^{133}Cs, ^{139}La, ^{175}Lu, ^{181}Ta, ^{187}Re, ^{193}Ir, ^{197}Au, ^{205}Tl, and ^{209}Bi, homonuclear COSY offers excellent possibilities, as shown in the case of ^{11}B NMR of metallacarboranes[6] and ^{51}V NMR of aqueous molybdovanadates.[7] High natural abundance is not, however, absolutely necessary, as shown by Domaille in 2-D INADEQUATE ^{183}W NMR studies of heteropolymetalates[8] (natural abundance 14.28 %, see Ref. 1, p. 192).

Experimental

All multinuclear magnetic resonance measurements were performed on a JEOL GSX-270 FT NMR spectrometer at 30 °C unless otherwise stated by using a 10 mm diameter tunable probehead.

^{15}N NMR spectra were recorded at 27.3 MHz using an INEPT pulse sequence to enhance the sensitivity of protonated nitrogens. In the case of compounds containing NO_2-groups, the pulse repetition rate was kept at at least 30 s to obtain full relaxation. The spectral resolution was better than 0.5 Hz and 1000—5000 scans were collected for every spectrum. ^{15}N chemical shifts were measured in reference to the signal of nitromethane measured in a 10 mm NMR tube. All the ^{15}N NMR parameters have been reported earlier.[9,10]

^{17}O NMR spectra were recorded at 36.5 MHz by using a proton broad band decoupling (BBD) pulse sequence with a 0.1 acquisition time and without any time delay. The spectral resolution was better than 9 Hz and the number of scans varied from 50,000 to 500,000 depending on the sample concentration. ^{17}O chemical shifts were referenced to the signal of a D_2O capillary tube inserted coaxially inside the 10 mm sample tube. The ^{17}O NMR parameters have been reported earlier.[11—19]

^{51}V NMR spectra were recorded at 70.9 MHz without proton decoupling using a 0.1 s acquisition time without any pulse delay. The spectral resolution was better than 9 Hz and the number of scans was 2000, corresponding to 4 min total measuring time. ^{51}V chemical shifts were referenced to the signal of the main peak of an aqueous solution of $NaVO_3$ (1000 mg/L, 30 °C, 10 mm tube).

^{77}Se NMR spectra were recorded at 51.4 MHz using a proton broad band decoupling (BBD) pulse sequence with a 0.4 s acquisition time and a 3 s pulse delay. The spectral resolution was 3 Hz and the number of scans was more than 10,000. ^{77}Se chemical shifts were referenced to the signal of a $(CH_3)_2Se$ measured in a 10 mm NMR tube at 30 °C.

^{119}Sn NMR spectra were recorded at 100.6 MHz without proton decoupling using a 1.5 s acquisition time and a 10 s pulse delay. The spectral resolution was 3 Hz and the number of scans varied from 1000 to 10,000 depending on the sample concentration. ^{119}Sn chemical shifts were referenced to the

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signal of a $(CH_3)_4Sn$ capillary tube inserted coaxially inside the 10 mm sample tube.

Results and Discussion

In a limited paper it is impossible to cover exhaustively the diverse applications of multinuclear magnetic resonance spectroscopy. Therefore only some examples of our investigations using multinuclear NMR are given.

^{15}N NMR. In spite of the low natural abundance of the ^{15}N isotope ^{15}N NMR spectroscopy was shown to be useful in structural studies of various nitrogen containing organic compounds.[20] From this point of view nitraminopyridines form an interesting group of compounds.[9,10] The exceptional properties of the nitramino substituent are explained by the remarkable double bond character[10] of the N—N bond.

^{17}O NMR. During recent years ^{17}O NMR at the natural abundance of ^{17}O (0.037 %, see Ref. 1, p. 92) has received considerable attention.[21—23] Environmentally important oxygen-containing chlorinated aromatics form an interesting topic for investigations by this method. Therefore chlorinated anisoles,[11] veratrols and trimethoxybenzenes,[12] benz- and salicylaldehydes,[13] vanillins[14] and protocatechualdehydes[15] have been the subject of our intensive ^{17}O NMR spectroscopic studies.

These works reveal the usefulness of ^{17}O NMR in the conformational analysis of methoxyl[11,12] and formyl[14] groups, in studying intramolecular hydrogen bonding,[13] and in estimating the tautomerism and resonance interactions of substituents with an aromatic ring.[15] In addition, ^{17}O NMR turned out to be an excellent way to investigate the keto-enol tautomerism in isomeric hydroxypyridines.[16]

Benzylidenemalonaldehydes are an interesting subject from the point of view of conformational analysis.[17] ^{17}O NMR was shown to be useful in estimating the conformational characteristics of these multirotor compounds.[18]

In addition to ^{13}C NMR spectroscopy (see Ref. [24]), ^{17}O NMR has been used in the field of organometallic compounds.[19,25,26] In the case of mesitylene transition metal carbonyls,[19] ^{17}O NMR spectroscopy showed surprisingly narrow line widths and good sensitivity. Therefore this method has exceptionally high potential in this field of chemistry.

^{51}V NMR. The ^{51}V nucleus has properties that make it the most suitable one for NMR detection among the transition metals in terms of its detectability (see Ref. 2, p. 18—58). For example $[VO_4]^{3-}$, $[HVO_4]^{2-}$, $[H_2VO_4]^-$, and various polyvanadates can easily be differentiated and quantified by ^{51}V NMR spectroscopy.[27]

^{77}Se NMR. Selenium can replace sulfur in many compounds and thus serves as a useful NMR probe instead of sulfur, which has poor NMR characteristics (see Ref. 1, p. 105). ^{77}Se NMR spectroscopy has been used in studying diselenaquinquephenylophanes.[28]

^{119}Sn NMR. Tin has two $I = 1/2$ isotopes, ^{117}Sn (natural abundance 7.61 %) and ^{119}Sn (8.58 %). It is therefore very easy to observe by NMR, and ^{119}Sn is generally preferred (see Ref. 2, p. 169). Plenty of experimental ^{119}Sn NMR data have been obtained.[29] Our interest is mainly focused on developing analytical methods for phenolic compounds by using their TBTO derivatives and ^{119}Sn NMR.[30]

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Multinuclear magnetic resonance spectroscopy has an enormous variety of uses in hetero-organic chemistry because it is possible to use different nuclei, different measuring techniques, and even different phases of a sample. Therefore one can conclude that multinuclear magnetic resonance spectroscopy is the most versatile method in this field of chemistry.

References

1. C. Brevard and P. Granger, *Handbook of High Resolution Multinuclear NMR*, John Wiley & Sons, New York, 1981.
2. *Transition Metal Nuclear Magnetic Resonance*, Ed. P. S. Pregosin; *Studies in Inorganic Chemisry*, Elsevier Science Publishers B.V., Amsterdam, 1991.
3. R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions,* Clarendon Press, Oxford, 1987.
4. A. Bax, *Two-Dimensional Nuclear Magnetic Resonance in Liquids,* Delft University Press, Delft, Holland, 1984.
5. D. Neuhaus and M. Williamson, *The Nuclear Overhauser Effect in Structural and Conformational Analysis,* VCH Publishers, New York, 1989.
6. T. L. Venable, W. C. Hutton, and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, **106**, 29.
7. O. W. Howarth, L. Petterson, and I. Andersson, *J. Chem. Soc., Dalton Trans.*, 1991, 1799 (and references).
8. P. J. Domaille, *J. Am. Chem. Soc.*, 1984, **106**, 7677.
9. E. Kolehmainen, K. Laihia, K. Rissanen, D. Rasala, and R. Gawinecki, *Magn. Reson. Chem.*, 1991, **30**, 527.
10. E. Kolehmainen, K. Laihia, D. Rasala, and R. Gawinecki, *Magn. Reson. Chem.*, in press.
11. E. Kolehmainen and J. Knuutinen, *Magn. Reson. Chem.*, 1988, **26**, 1112.
12. J. Knuutinen and E. Kolehmainen, *Magn. Reson. Chem.*, 1990, **28**, 315.
13. E. Kolehmainen and J. Knuutinen, *Magn. Reson. Chem.*, 1991, **29**, 520.
14. E. Kolehmainen, K. Laihia, J. Knuutinen, and J. Hyötyläinen, *Magn. Reson. Chem.*, 1992, **30**, 253.
15. E. Kolehmainen, K. Laihia, and J. Hyötyläinen, *Magn. Reson. Chem.*, in press.
16. E. Kolehmainen, K. Laihia, D. Rasala, and R. Gawineski, *Magn. Reson. Chem.*, 1991, **29**, 878.
17. E. Kolehmainen, R. Laatikainen, and V. Král, *Magn. Reson. Chem.*, 1986, **24**, 498 (and references).
18. E. Kolehmainen and V. Král, *Magn. Reson. Chem.*, 1990, **28**, 751.
19. E. Kolehmainen, K. Laihia, M. I. Rybinskaya, V. S. Kaganovich, and Z. A. Kerzina, *J. Organomet. Chem.*, in press.

20. G. C. Levy and R. L. Lichter, *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*, John Wiley & Sons, New York, 1979.
21. J.-P. Kintzinger, *Oxygen NMR. Characteristic Parameters and Applications in NMR 17. Basic Principles and Progress. Oxygen-17 and Silicon-29.* Springer Verlag, Berlin, 1981.
22. D. W. Boykin and A. L. Baumstark, *Tetrahedron Report, Number 253, Tetrahedron*, 1989, **45**, 3613.
23. *^{17}O NMR Spectroscopy in Organic Chemistry,* Ed. D. W. Boykin, CRC Press, Boca Raton, Florida, 1991.
24. B. E. Mann and B. F. Taylor, *^{13}C NMR Data for Organometallic Compounds,* Academic Press, London, 1981.
25. J. P. Hickey, J. R. Wilkinson, and L. J. Todd, *J. Organomet. Chem.*, 1979, **179**, 159.
26. (a)S. Aime, L. Milone, D. Osella, G. E. Hawkes, and E. W. Randall, *J. Organomet. Chem.*, 1979, **178**, 171; (b)S. Aime, L. Milone, D. Osella, G. E. Hawkes, and E. W. Randall, *J. Am. Chem. Soc.*, 1981, **103**, 5920; (c)S. Aime, L. Milone, D. Osella, and E. Sappa, *Inorg. Chim. Acta*, 1978, **29**, L211.
27. E. Kolehmainen and A. Mikkonen, *in XVI National NMR Symposium, Abstracts*, Abo Akademi, Finland, June 1993.
28. K. Airola, E. Kolehmainen, K. Rissanen, and R. Kauppinen, *XVI National NMR Symposium, Abstracts*, Abo Akademi, Finland, June 1993.
29. R. K. Harris and B. E. Mann, *NMR and the Periodic Table*, Academic Press, London, 1978.
30. E. Kolehmainen, L. Paasivirta, R. Kauppinen, T. Otollinen, S. Kasa, and R. Herzschuh, *Intern. J. Environ. Anal. Chem.*, 1990, **43**, 19.

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