MAGNETIC RESONANCE IN CHEMISTRY
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# Guest Editorial: NMR Spectroscopy of Hydrogen-Bonded Systems

Since the early years of NMR spectroscopy, this technique has been used to study hydrogen transfer and bonding, which are elementary phenomena important in nature. The NMR interactions exploited were mainly chemical shifts and scalar couplings, but also dynamic effects such as lineshape changes and relaxation gave interesting information. Handicaps of NMR were and often still are the limited dynamic range, which make studies of proton and hydrogen bond exchange difficult. However, in recent decades, more-dimensional multinuclear NMR has made tremendous progress in the study of solids, liquid–solid hybrid systems, soft matter, biomolecules and living systems. Quantum-mechanical computational techniques allow us today to predict NMR parameters with high precision. Hence it is not surprising—although not well known—that because of its high selectivity, NMR plays an increasing role in hydrogen bond research of a growing number of complex systems. Improved techniques are currently used to study not only the structure but also the function and the dynamics of hydrogen bonded systems, ranging from simple molecules to enzymes. On the other hand, the new **Hydrogen Bond NMR** becomes a motor for the development of NMR techniques.

The scope of this Special Issue of *Magnetic Resonance in Chemistry* is to provide in a series of 24 experimental and theoretical papers some snapshots of **Hydrogen Bond NMR**. The issue starts in Section A with a series of papers concerning the 'Structure and Dynamics of Hydrogen Bonded Solids.' Here, especially dipolar NH and ND couplings of biological model systems are studied and related to the world of chemical shifts. Such isotope effects provide interesting insights into the proton potentials. They can arise both from anharmonic proton motions and from isotope effects on tautomeric equilibria. The latter can be detected by high-resolution solid-state NMR. The dynamics of protons and deuterons in cyclic hydrogen bonded systems and hydrogen bonded chains can be studied using solid-state longitudinal relaxometry up to the micro- and nanosecond time-scale, as in solids interference with molecular reorientations, generally does not occur.

The next series of papers, in Section B, are devoted to the 'Structure and Dynamics of Systems with Single Hydrogen Bonds in the Liquid State.' The problem of the localization and transfer of the proton in acid–base complexes is studied by a combination of chemical shift and relaxometry, and in the case of intramolecular complexes by the measurement of deuterium isotope effects on $^{13}C$ and $^{15}N$ chemical shifts. An important task is to elucidate the origin of these hydrogen bond isotope effects, which are strongly influenced by the solvent. Using novel low-temperature NMR methods where deuterated gases are employed as NMR solvents, the regime of slow hydrogen bond exchange can be reached such that different hydrogen bonded species can be distinguished and the effect of dimerization on the hydrogen bond structure studied. In this regime, also intrinsic primary and secondary H/D isotope effects, the effect of the solvent polarity and novel scalar couplings across hydrogen bonds are observed. Two papers, an experimental and a theoretical one, are devoted to the relation between $J(^1H,^{15}N)$ and $J(^{15}N,^{15}N)$ coupling constants and the geometry of NHN hydrogen bonds. Finally, $J(^1H,^1H)$ couplings across hydrogen bonds are calculated in order to detect intramolecular hydrogen bonding in carbohydrates.

The complexity of the systems is increased in the papers in Section C on 'Hydrogen Bonding in Molecular Liquids and Mesoporous Systems.' For a molecular hydrogen bonded liquid such as *N*-methylacetamide correlations between structural, NMR and IR spectroscopic properties are calculated and compared with experiments. The interplay between hydrogen bonding and hydrophilicity affects the reorientational dynamics in solution. When chemical shifts do not allow us to determine association, chemical shift resolved diffusion coefficient measurements (DOSY) give interesting insights into the nature of hydrogen bonded complexes. Diffusion coefficient measurements also reveal the effects of hydrogen bonding of pyridine with surface OH groups in the inner pores of mesoporous silica.

The final series of papers, in Section D, are devoted to the study of 'Hydrogen Bonds in Biomolecules.' Model systems are developed in order to study substituent effects on the N—H···N hydrogen bonds in duplex DNA and the new field of scalar couplings across hydrogen bonds in these types of molecules is reviewed. A novel technique is proposed to obtain such couplings via $^1H–^1H$ correlated spectroscopy. Another new field is the study of C—H···O hydrogen bond interactions in DNA. Using low-temperature NMR techniques, hydrogen bonding in complexes of modified adenosine and 4-thiouridine complexes can be studied. *Ab initio* computational methods are now so much advanced that they can be applied to reproduce

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the Karplus relations for model peptides. Finally, two contributions review the area of the role of strong hydrogen bonding in model systems and enzymatic complexes as well in the active sites of enzymes such as serine protease.

This issue does not have the ambition to provide a comprehensive description of all activities of **Hydrogen Bond NMR**, but its goal is to promote this interesting field which provides a unique link of quantum chemistry and quantum biology. It remains to thank all contributors who readily accepted my invitation to present results from their laboratories and who thus made this interesting Special Issue possible.

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# Editorial

Among the variety of chemical bonds, the *hydrogen bond*, which, because of its general structure X—H···Y, is also called *hydrogen bridge*, has a unique position because it is much weaker than classical chemical bonds but at the same time has a much broader distribution in both liquids and solids than any other bond. In particular, its role in biochemistry gives the hydrogen bond outstanding importance and has strengthened the interest in its physical and chemical properties. Intriguing questions, e.g. is the hydrogen bond linear?; what is the position of the hydrogen atom?; is the bond static or dynamic?, have motivated much experimental and theoretical research effort. The earliest spectroscopic technique available to the experimentalist was, of course, IR spectroscopy, which is still an important tool today. With the advent of NMR spectroscopy, a powerful new method became available, especially since proton NMR was the dominant technique at the beginning. Over the years, the different NMR techniques have been applied with great success to the study of hydrogen bond phenomena, and the introduction of new and more sophisticated NMR techniques in recent years has produced impressive results. It was therefore desirable to devote a Special Issue to 'NMR Spectroscopy of Hydrogen-Bonded Systems' in order to give an overview of the state of the art. We are most grateful to Professor H.-H. Limbach, one of the leading NMR spectroscopists in this field, for readily accepting our invitation to act as Guest Editor. He was able to attract a large number of renowned authors as contributors and the result is an excellent collection of articles that treat various aspects of the subject. Our thanks go to the Guest Editor and all the authors for their efforts which made this issue possible. As on similar occasions, our Production Department contributed with its skill to the success. I wish our readers interesting and illuminating reading.

**H. Günther**
Editor-in-Chief

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## Hydrogen Bonding in Molecular Liquids and Mesoporous Systems

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S149-S157 **Stray field gradient NMR reveals effects of hydrogen bonding on diffusion coefficients of pyridine in mesoporous silica**
E. Gedat, A. Schreiber, G. H. Findenegg, I. Shenderovich, H.-H. Limbach, G. Buntkowsky
Abstract PDF Full Text (Size: 220K)
**Published Online:** 5 Nov 2001
**DOI** 10.1002/mrc.932

## Hydrogen Bonds in Biomolecules

S159-S165 **Developing model systems for the NMR study of substituent effects on the N - H···N hydrogen bond in duplex DNA**
Rei Ishikawa, Chojiro Kojima, Akira Ono, Masatsune Kainosho
Abstract PDF Full Text (Size: 167K)
**Published Online:** 5 Nov 2001
**DOI** 10.1002/mrc.941

S166-S170 **Applications of $^{1}H_{a}$-$^{1}H_{d}$ correlated $^{2h}J$(N,N) spectroscopy for identifying $H_{a}$ - C - $N_{a}$···$H_{d}$ - $N_{d}$ hydrogen bonds in nucleic acids**
Ananya Majumdar
Abstract PDF Full Text (Size: 255K)
**Published Online:** 5 Nov 2001
**DOI** 10.1002/mrc.947

S171-S176 **Investigation of the energetics of C  H···O hydrogen bonds in the DNA i-motif *via* the equilibrium between alternative intercalation topologies**
Jean-Louis Leroy, Karim Snoussi, Maurice Guéron
Abstract PDF Full Text (Size: 195K)
**Published Online:** 5 Nov 2001
**DOI** 10.1002/mrc.935

S177-S182 **Hydrogen bonding in complexes of adenosine and 4-thiouridine: a low-temperature NMR study**
Eline M. Basilio Janke, Anita Dunger, Hans-Heinrich Limbach, Klaus Weisz
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**Published Online:** 5 Nov 2001
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S183-S189 **A correlated *ab initio* study of Karplus relations for model peptides**
S. Ajith Perera, Rodney J. Bartlett
Abstract PDF Full Text (Size: 148K)
**Published Online:** 5 Nov 2001
**DOI** 10.1002/mrc.911

S190-S198 **Review: Strong hydrogen bonding in molecules and enzymatic complexes**
Perry A. Frey
Abstract PDF Full Text (Size: 168K)
**Published Online:** 5 Nov 2001
**DOI** 10.1002/mrc.953

S199-S213 **Review: Contributions of NMR spectroscopy to the study of hydrogen**

**bonds in serine protease active sites**
William W. Bachovchin
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