Editorial

The notion of the hydrogen bond has been invented at the beginning of our century and was used by *Latimer* and *Rodebush* in 1920, and independently by *Huggins* in 1922, to characterize a structural regularity in which a hydrogen atom is bound to two neighbors. Almost forgotten in the following 15 years, the hydrogen bond was brought again into the focus of interest when it was 'rediscovered' as a regularity in crystal structures. The development of efficient computational methods in quantum chemistry provided new tools for the analysis of intermolecular forces. This novel approach was used extensively in the seventies to develop a heuristic theoretical concept for the hydrogen bond which allowed to derive quantitative expressions for different contributions, like the electrostatic energy, exchange repulsion energy, polarization energy, and dispersion contribution or charge transfer energy. In principle, charge transfer can also be interpreted as a covalent contribution. Later on very successful developments of computational methods yielded results that were in qualitative agreement with the existing concept and the available experimental data. More recently, it became possible to reach an unforeseeable accuracy in *ab intio* calculations that laid down the basis for successful competition with experimental results from vapor phase spectroscopy. Progress in the experimental techniques for the study of intermolecular complexes, in particular small hydrogen-bonded clusters, was made through molecular beam electronic resonance spectroscopy and application of infrared laser spectroscopy.

In recent years, the major impact in the understanding of hydrogen bonds came from studies on clusters of few to many molecules. The primary issue of investigations on these systems is to obtain precise information of the nature and the extent of deviations from pairwise additivity that is often addressed as hydrogen bond cooperativity. Another problem that had intrigued theorists for a long time is the stability of intramolecular hydrogen bonds. Coupling of these hydrogen bonds to π-electrons, in particular to conjugated π-electron systems, increases substantially their stability, whereas no major effects are observed in absence of conjugation partners. Progress in computational capacities and experimental techniques provided tools that nowadays allow to study and to analyze these subtle phenomena with sufficient reliability.

This issue of *Chemical Monthly* presents a collection of review articles and original papers devoted to hydrogen bonding. Without the claim of full coverage they also contain a representative overview of the research work done in this area at the Austrian universities.

The review of *Schuster* and *Wolschann* aims at a presentation of the state of the art in hydrogen bonding with the ultimate goal to understand the hydrogen bonds in biopolymers.

NMR spectroscopy is one of the most powerful tools to detect and to investigate hydrogen bonds. Recent developments in the methodology of NMR spectroscopy allow to study hydrogen bonding in aqueous solution. The review by *Konrat*, *Tollinger*, *Kontaxis*, and *Kräutler* describes the new techniques and presents interesting examples, thus demonstrating the power of the approach.

In a class of *Mannich* bases derived from substituted phenols or naphthols, stable hydrogen bonds are formed in a six-membered ring containing an sp^3 hybridized carbon atom. These rings contain a hydrogen bond without coupling to conjugated π-electrons and hence represent excellent model systems for case studies on intramolecular hydrogen bonding (*Koll*, *Wolschann*).

Simperler and *Mikenda* study competition between intramolecular hydrogen bonds in substituted phenols with carbonyl groups in positions 2 and 6.

Cyanodiacetylene can adopt two modes of intermolecular interaction in the dimer: hydrogen bonding or antiparallel orientation with a compensation of the dipole moments. The contribution by *Karpfen* shows that accurate calculations clearly favor the latter arrangement.

The paper by *Wolf et al.* presents a molecular dynamics study on proton transfer in coupled pairs of hydrogen bonds. Two representative examples are chosen: the formic acid dimer and 5,8-dihydroxy-1,4-naphthoquinone. The essential difference between the two cases concerns the double proton transfer which is a concerted process in the carboxylic acid dimer, but a consecutive two-step process in the second example.

The paper by *Libowitzky* provides a comparison of $OH\cdots O$ bond lengths and OH stretching frequencies in a set of data derived from 65 minerals. The correlation curve shows a strong dependence for short hydrogen bonds, smoothly converging into a constant vibrational frequency for hydrogen bonds with an OO-distance of 3.0 Å or longer.

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