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INTRODUCTION: WEAK NONCOVALENT INTERACTIONS

The development of chemistry in the last 20 years has revealed a significant shift of interest on the part of theoreticians and experimentalists [1,2]. Earlier, chemists' attention was concentrated on atoms and atom–atom bonds. This strategy has been very successful in the creation of new molecules with unusual structures and with new chemical and physical properties. However, two decades ago, the primary objects of chemical studies become intermolecular interactions leading to complex molecular assemblies that exhibit unusual and often unique macro properties. This situation has dominated in all areas of modern chemical science: from physical, organic, inorganic, and organometallic chemistry to material science and biochemistry, and has resulted in the formulation of new chemical disciplines: supramolecular chemistry and crystal engineering.

As is well known, molecular assemblies can be created due to secondary and weak interactions referred to as *noncovalent bonding*. This term implies that such bonding *does not lead to the formation of new two-electron σ -bonds*. In this context, the formation of new σ -bonds symbolizes strong interactions that change molecular skeletons and therefore require significant energy. In contrast, *noncovalent synthesis* proceeds through the formation and rupture of secondary interactions between molecular subunits. Since the covalent skeletons of initial molecules are not affected, this synthesis occurs at the other end of the energy scale [1]. On this scale, small energies often act against entropies that complicate the synthesis. However, if noncovalent interactions are cooperative, thermodynamically spontaneous supramolecular aggregation finally provides a significant energy gain.

If the utilization of weak noncovalent interactions leading to molecular aggregations is a general principle in supramolecular chemistry, and periodicity is a general prerequisite in the crystalline state, then periodically distributed noncovalent interactions constitute the basis of molecular crystal engineering [1]. In other words, molecular crystal engineering can be considered as supramolecular solid-state chemistry, again based on weak noncovalent interactions.

Finally, mastering secondary noncovalent interactions is important not only for supramolecular chemistry and crystal engineering, but controlling these forces is fundamental in the context of an understanding of complex biological processes, particularly the principles and mechanisms of molecular recognition [1–3].

The attractive forces that can hold molecules together include van der Waals interaction, electrostatic attraction (when molecules are charged or polar), and hydrogen bonding. Since there is no clear border between a very weak hydrogen bond and van der Waals interaction, the latter requires some explanation.

It is well known that neutral and nonpolar molecules push each other away when the distance between them is small but are attracted to each other at longer distances. This idea was suggested in the second half of the nineteenth century to rationalize the kinetic behavior of gases. Then van der Waals formulated an equation according to which molecules in the gas phase undergo the influence of an attractive force field. The latter explains the existence of the condensed phase as a result of intermolecular attractive forces. These interactions are very weak and can be estimated as 10^{-2} to 10^{-1} kcal/mol per one van der Waals contact. At the same time, these interactions are long, act at long intermolecular distances, and form a van der Waals potential energy surface. Intermolecular potentials cannot be measured directly, but they associate with the spectra of van der Waals complexes: The intermolecular modes of the van der Waals complexes depend directly on the potentials that hold these complexes [4,5]. It is worth mentioning that when other intermolecular attractive forces are weak, the van der Waals modes, being very soft, have large amplitudes. Their frequencies can be estimated as a *few tens* of reciprocal centimeters for complexes containing nonpolar monomers [5]. By comparison, frequencies in hydrogen-bonded systems are a *few hundreds*. Experimentally, the van der Waals modes can be detected directly by laser-based far-infrared (IR) spectroscopy or as sidebands in mid-IR and ultraviolet (UV) spectra. IR spectroscopy of cold gases can also provide useful information on van der Waals complexes.

Molecular systems formed by van der Waals forces can usefully be characterized by zero-electron kinetic-energy photoelectron (ZEKE) and resonance-enhanced multiphoton ionization (REMPI) spectroscopy. For details, readers are referred to ref. 4, where the complexes formed by phenol and argon are of particular interest. In fact, these spectroscopic methods can show transitions from van der Waals interaction to hydrogen bonding. Figure 1.1 illustrates a van der Waals complex, phenol • Ar, where the distance between the argon atom and the center of the aromatic ring is as long as 3.58 Å. The structure shown in Figure 1.1(b) corresponds to a hydrogen-bonded complex. Ab initio calculations have predicted the existence of several isomeric structures for this phenol • Ar system, two of which are characterized by the lowest energies (Figure 1.1). In contrast, REMPI and ZEKE spectra only support van der Waals structure existing under supersonic jet conditions.

Among intermolecular attractive forces, hydrogen bonding is the shortest in terms of intermolecular distance but the most energetically strong. In fact, a hydrogen bond can provide an energy gain per structural unit from 2.4 kcal/mol to

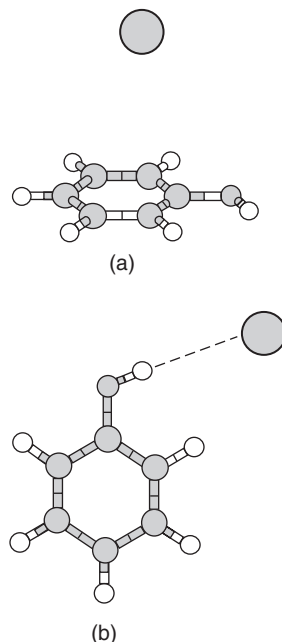


Figure 1.1 (a) Van der Waals complex formed by phenol and argon molecules; (b) corresponding hydrogen-bonded complex. (Reproduced with permission from ref. 4.)

24 kcal/mol, or even more in the case of charge-assisted hydrogen bonds [6]. By comparison, the dipole–dipole interaction energy, for example, between even the very polar molecules HCl is only 0.8 kcal/mol. It is obvious that hydrogen bonds as well as dihydrogen bonds are most perspective for creation of supramolecules from molecular subunits.

Hydrogen bonding is one of the oldest and most fundamental concepts in chemistry [7]. Hydrogen bonds are found in solids, in liquids, and in the gas phase and often dictate aggregate states of chemical compounds, classical examples being H_2S (gas) and H_2O (liquid) molecules. The hydrogen bonds define the crystal packing of organic and organometallic molecules [2], modulate the reactivity of groups within molecules, and stabilize conformational and configurational molecular states [7]. The role of hydrogen bonding is well recognized in the stabilization of complex biological macromolecules, enhancing the selectivity binding of substrates to these biological molecules. Finally, hydrogen bonding plays a very important role in proton transfer reactions.

The concept of hydrogen bonding is constantly evolving from classical hydrogen bonds to nonclassical (or nonconventional) hydrogen-bonded complexes. Here, on the basis of new experimental and theoretical data and new approaches to this problem, the nature of a proton-donor component and a proton-acceptor site is reformulated completely. In addition, experimental criteria that have been used successfully earlier for the detection of hydrogen bonds are also changed.

For example, due to their elongations, the *red shifts* of vibrational modes observed for proton-donating bonds (e.g., O–H, N–H) were the strongest evidence of a hydrogen-bond interaction. However, since the discovery of *blue-shifting interactions* [8], where the proton-donating bond is *shortened* upon complexation, the experimental formulation of hydrogen bonds has changed completely.

Among the various nonconventional hydrogen bonds, dihydrogen bonds are the most unusual and intriguing. These bonds are formed between two hydrogen atoms, the first positively charged and acting as a proton-donor component, the second negatively charged and acting as a proton-acceptor site:



The first reliable data on the existence of such bonds within crystal structures came from the mid-1990s [9], when Wessel and co-workers reported on the unusually-short intermolecular contacts B–H \cdots H–N. Nowadays, studies in this fast-developing field involve a large number of chemical elements participating in the bonding quartet X–H \cdots H–Y. It is clear now that this unusual bonding plays an important role as an organizing interaction in molecular architecture (intramolecular dihydrogen bonds), in molecular aggregations (intermolecular dihydrogen bonds), and in the reaction ability of molecules.

The aim of the book is to show (1) a diversity of dihydrogen bonds; (2) the nature, geometry, energetics, and dynamics of these bonds; and (3) the factors that control the energy of dihydrogen bonds from very weak to very strong.

Since it is very important recognize the place of dihydrogen bonding among various noncovalent interactions and to show differences between hydrogen and dihydrogen bonds as well as their similarity, we begin Chapter 2 with a brief description of hydrogen bonds, their classification, their energy, geometry parameters, and dynamics. For details the reader is referred to numerous scientific reviews and monographs, among which refs. 10 to 19 are notable.

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