

Editorial

Analysis of Hydrogen Bonds in Crystals

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Abstract: The determination of crystal structures provides important information on the geometry of species constituting crystals and on the symmetry relations between them. Additionally, the analysis of crystal structures is so conclusive that it allows us to understand the nature of various interactions. The hydrogen bond interaction plays a crucial role in crystal engineering and, in general, its important role in numerous chemical, physical and bio-chemical processes was the subject of various studies. That is why numerous important findings on the nature of hydrogen bonds concern crystal structures. This special issue presents studies on hydrogen bonds in crystals, and specific compounds and specific H-bonded patterns existing in crystals are analyzed. However, the characteristics of the H-bond interactions are not only analyzed theoretically; this interaction is compared with other ones that steer the arrangement of molecules in crystals, for example halogen, tetrel or pnictogen bonds. More general findings concerning the influence of the hydrogen bond on the physicochemical properties of matter are also presented.

Keywords: hydrogen bond; crystal structure; quantum chemical calculations; noncovalent interactions

1. Introduction

Numerous important findings concerning the hydrogen bond are related to crystal structures. For example, one of the first definitions of the hydrogen bond was proposed by Pauling in his monograph on the chemical bond, and it is as follows: “Under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is called the hydrogen bond” [1]. Pauling also has pointed out that the hydrogen atom is situated between the most electronegative atoms and that it usually interacts more strongly with one of them, forming the covalent bond; the other interaction of hydrogen with the next electronegative atom is much weaker and mostly electrostatic in nature. It is important that Pauling, describing the hydrogen bond, refers directly to crystal structures, to fluorine compounds, to clathrate compounds, and to structures of alcohols or carboxylic acids. He describes the effect of the hydrogen bond on the physical properties of substances, and in detail, the cooperativity H-bond effects in crystals, particularly the cooperativity in HF and HCN compounds (the term “cooperativity” that appeared later in the literature does not occur in this monograph; however, exactly this phenomenon was described and discussed [1]).

One can mention other important monographs; however, this case is completely concerned with the hydrogen bond and mainly addresses the crystal structures, including the monographs of Pimentel and McClellan [2], Jeffrey and Saenger [3], Jeffrey [4], Desiraju and Steiner [5], Nishio, Hirota and Umezawa [6] or Gilli and Gilli [7]. It is important that the monographs describing mostly the theoretical studies on the hydrogen bond refer to the experimental results, among them crystal structures [8,9]. Furthermore, even important monographs are mentioned here since the hydrogen bond interaction was and is the subject of a huge number of studies.

2. From a Variety of Hydrogen Bond Interactions to New Definitions of the Hydrogen Bond

The Pauling definition of a hydrogen bond (HB) was cited in the previous section [1]; it is worth mentioning that further modifications of this definition were mainly inspired by findings concerning crystal structures. For example, the article introducing and explaining the recent definition recommended by IUPAC often refers to properties of the hydrogen bond that are revealed in crystal structures, and one may mention the directionality of the hydrogen bond [10]. This definition states that: “The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.”

One of the first debates on hydrogen bonds was based on the nature of interactions in crystal structures [11,12]. It was contested that for HB, the hydrogen atom has to be located only between electronegative centers; the C–H ... O interactions were classified as HBs [11]. Several years later, Taylor and Kennard applied subtle statistical methods to analyze numerous crystal structures and they proved that the C–H ... Y (Y designates the Lewis base center) interactions possess characteristics of typical hydrogen bonds [13]. After that it was commonly accepted that the carbon atom may be the proton-donating center in HB systems. Also π -electrons of these systems such as acetylene, ethylene and their derivatives or π -electrons of aromatic systems were classified as possible proton acceptors (Lewis bases) in HBs [6].

The detailed analysis and description of a new kind of hydrogen bond, the dihydrogen bond (DHB), was based on the detection of such interactions in crystal structures [14]. This interaction is characterized by the contact between two H atoms of opposite charges, *i.e.*, one H atom plays the role of the Lewis acid and the other one acts as the Lewis base; Figure 1 shows the fragment of the structure with the Re–H ... H–N dihydrogen bond.

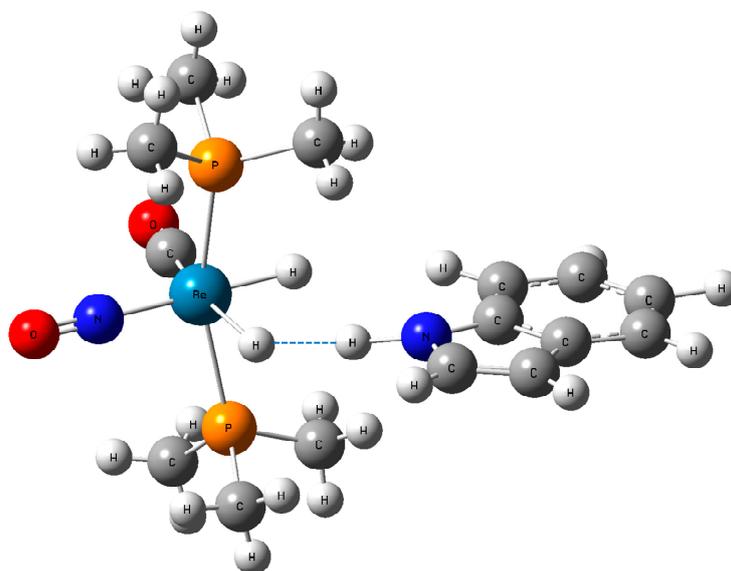


Figure 1. The fragment of the crystal structure of the $\text{ReH}_2(\text{CO})(\text{NO})(\text{PMe}_3)_2$ complex with indole; the H ... H contact corresponding to the Re–H ... H–N dihydrogen bond is designated by the blue broken line. The structure was taken from the Cambridge Structural Database [15]; refcode: XATFAZ, following Reference [16].

The above-mentioned IUPAC definition of the hydrogen bond covers the C–H ... Y interactions and those where π -electrons play the role of the Lewis base and the dihydrogen bonds; other interactions possessing numerous characteristics of “the typical Pauling-style HBs” are classified as HBs according to this definition. It is mentioning that the DHB interaction may be treated as a

preliminary stage of the reaction leading to the release of the molecular hydrogen; it is important that this process was analyzed in crystal structures, *i.e.*, the evidence of the topochemical control of this reaction was reported [17]. In general, HBs may be treated as the preliminary stage of the proton transfer process; the proton transfer reactions in solid-state structures are often the subject of analysis, especially the double proton transfer which is characteristic for carboxylic acids linked in dimers by two, often equivalent $C=O \dots H-O$ hydrogen bonds [18]. In such a way the eight-member ring is formed, characteristic not only for carboxylic acids but also for other species such as, for example, amides. Figure 2 presents examples of crystal structures where such motifs exist.

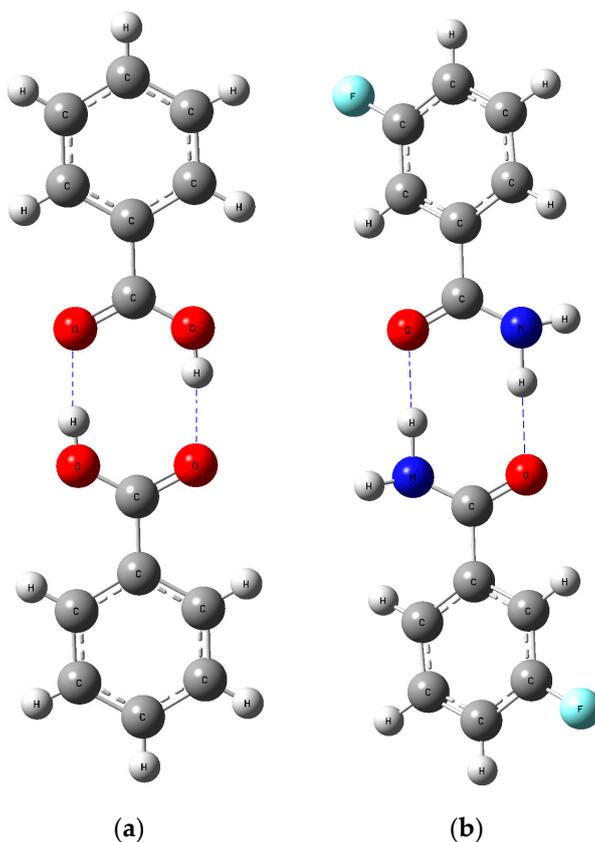


Figure 2. The fragments of the crystal structures of: (a) benzoic acid [19] where the dimer is linked by O-H ... O HBs; (b) m-fluorobenzamide [20] where the dimer is linked by N-H ... O HBs. The structures were taken from the Cambridge Structural Database [15]; refcodes: BENZAC02 and BENAFM10, respectively.

The method based on the graph theory was introduced by Etter *et al.* [21] and developed later by Bernstein *et al.* [22]; it allows the categorization of HB motifs. The motifs presented in Figure 2 are characterized by eight-member rings closed by two proton donors and two proton acceptors. The other approach proposed was where the supramolecular synthons as the basic molecular entities may form, in a predictable manner, large assemblies such as those in crystal structures [23].

New techniques and approaches used to determine crystal structures require additional comments. For example, the electron density can be reconstructed from diffraction experiments [24] with the use of X-rays or by more recently introduced γ -ray and synchrotron radiation techniques. Numerous interesting studies were performed where the electron density distribution analysis allows the description of inter- and intramolecular interactions, among them hydrogen bonds. It is also important that numerous theoretical approaches may be applied here, such as, for example, the Quantum Theory

of Atoms in Molecules which is a powerful approach to deepening the understanding of the nature of interactions [25].

3. Conclusions

One can mention numerous topics connected both with the HB interaction and with crystal structures; it is difficult to briefly mention all of the most important studies and findings. However, it is very important that several topics mentioned here earlier, which are the subject of extensive investigations, are represented in this special issue. This issue is a collection of important scientific contributions where new crystal structures are presented, where the physicochemical phenomena dependent on H-bond interactions are described and where the experimental results are supported by theoretical calculations; also, the hydrogen bonds are compared with other interactions that steer the arrangement of molecules in crystals.

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Conflicts of Interest: The author declares no conflict of interest.

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