



One Hundred Years After the Latimer and Rodebush Paper, Hydrogen Bonding Remains an Elephant!

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Abstract | Latimer and Rodebush (J Am Chem Soc 42: 1419–1433, 1920) discussed the ways a Lewis dot structure could be drawn for liquid water and proposed that the H held between two octets constitutes a bond in 1920. When it was realized that the other molecule of life, DNA, owes its double helix structure to specific hydrogen bonds between A–T (two) and C–G (three) base pairs, the interest in hydrogen bonding grew dramatically. While hydrogen bonding could be readily seen in water and DNA, it was not so easy to understand leading to continuous debates about what it means. This article gives a personal perspective of the evolution of hydrogen bonding since the Latimer and Rodebush paper to the recent IUPAC definition of hydrogen bond, published in 2011 and now. Is there a third C–H...O hydrogen bond in the A–T base pair?

In the year 1920, Wendell M. Latimer and Worth H. Rodebush published a paper¹ in the *Journal of the American Chemical Society* titled “Polarity and Ionization from the Standpoint of the Lewis Theory of Valence”. Reading this title today, it would not be obvious that this paper was credited by Linus Pauling in his classic book² as the first to mention hydrogen bond. Latimer and Rodebush start by discussing some previous work by Abegg and Bodlander³ on strong and weak electrolytes, in which they introduced a property called ‘electro-affinity’ for elements! They point out that this property was commonly designated as electronegative and electropositive character of an element and it was related to its position in the periodic table! However, their paper focuses on Lewis’s theory of ‘two dots’ (an electron pair) between two atoms as a bond,⁴ extended and renamed as covalent bond by Langmuir.⁵ Interestingly, the title of the paper by Lewis was “The Atom and the Molecules” and that of Langmuir was “The Arrangement of Electrons in Atoms and Molecules”. Latimer and Rodebush explored ‘associated liquids’ and they had to worry about how the molecules arrange themselves together in

condensed phase! They had no data from an X-ray diffractometer or any of the spectroscopic methods which were yet to be developed! They compared ammonia, water and hydrogen chloride.

Latimer and Rodebush wrote Ammonia adds a hydrogen readily but little tendency to give one up. Hydrogen chloride, on the other hand, shows just the opposite tendencies. Water occupies an intermediate position and shows tendencies to both add and give up hydrogen, which are nearly balanced. Then, in terms of the Lewis theory, a free pair of electrons from one water molecule might be able to exert sufficient force on a hydrogen held by a pair of electrons on another water molecule to bind the two molecules together. Structurally, this may be represented (as redrawn in Fig. 1). Such combination need not be limited to the formation of double or triple molecules. Indeed, the liquid may be made up of large aggregates of molecules, continually breaking up and reforming under the influence of thermal agitation. Such an explanation amounts to saying that the hydrogen nucleus held between 2 octets constitutes a weak “bond”.

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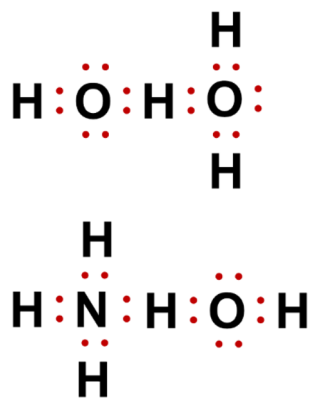


Figure 1: Lewis dot structures of $\text{H}_2\text{O}-\text{H}_2\text{O}$ and NH_4OH , redrawn, from Latimer and Rodebush paper⁶.

What is quoted above from the paper of Latimer and Rodebush displays remarkable insight and Pauling's choice of this paper as the first to mention hydrogen bond seems apt! Moreover, this same paragraph shows what is extraordinary about hydrogen bond! With their ability to accept and give up proton, ammonia and hydrogen chloride can form a hydrogen-bonded complex, which was investigated using a pulsed nozzle Fourier transform microwave spectrometer, 7 decades later.⁶ Latimer and Rodebush could predict this indirectly in proposing a structure of ammonium hydroxide, as also shown in Fig. 1. However, it is not clear if Latimer and Rodebush could have thought about NH_3 being a hydrogen bond donor⁷ or HCl being a hydrogen bond acceptor!⁸ They certainly did not think about CH_4 acting as both hydrogen bond donor and acceptor!⁹

Despite the remarkable insight about hydrogen bond, this paper by Latimer and Rodebush could at best be described as a sleeping dwarf, considering the fact that it has received about 250 citations in this decade. The citations over the last century are shown in Fig. 1. The data is taken from Google Scholar. That it was sleeping for seven decades is clear from the figure. It is growing in the recent decades and it is unlikely to be classified as a citation classic! Clearly, all the contributors to this special issue do not share this view and thought it fit to celebrate the 100th Volume of this Journal by bringing out this issue also celebrating the centenary of this paper. The importance of hydrogen bonding can be understood by the data, as given in Fig. 2. The number of papers published on 'hydrogen bond', (when chosen as a subject in a search) from the ISI Web

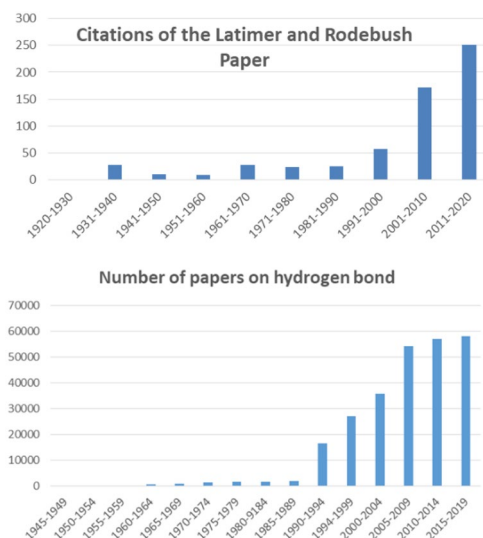


Figure 2: Number of citations received by the Latimer and Rodebush (top) paper based on Google Scholar and the number of papers on 'hydrogen bond' (bottom) from a search in Web of Science.

of Science is shown in this figure. In this decade, until 30 November 2019, a total of 115,087 papers have been published, about 32 papers per day. In 2011, when IUPAC published a technical report¹⁰ on hydrogen bonding, this figure was about 28 per day!

The interest in the paper by Latimer and Rodebush and on hydrogen bond grew exponentially after it was realized that the base pairs in DNA are bound by hydrogen bonds.^{11, 12} Adenine and thymine are bound by two hydrogen bonds and cytosine and guanine are bound by three hydrogen bonds, as shown in Fig. 3. Is there a third hydrogen bond in A–T base pair?

This is important to ensure that the genetic code is passed on nearly error-free, since life began on earth. That hydrogen bonding controls the essential properties of the molecules of life, water and DNA, was abundantly clear to everyone. However, what is hydrogen bonding was not so clear and from the early days it led to debates and controversies. The situation was and is comparable to the parable of an elephant and six blind men, beautifully sketched in the cover of this issue! The earliest versions of the parable are found in ancient Hindu/Buddhist/Jain texts, all originating from what is India today. Griffiths quotes from the Rig Veda: Reality is one, though wise men speak of it variously.¹³

My interest in hydrogen bonding was kindled by a comment from a referee received in 2004.

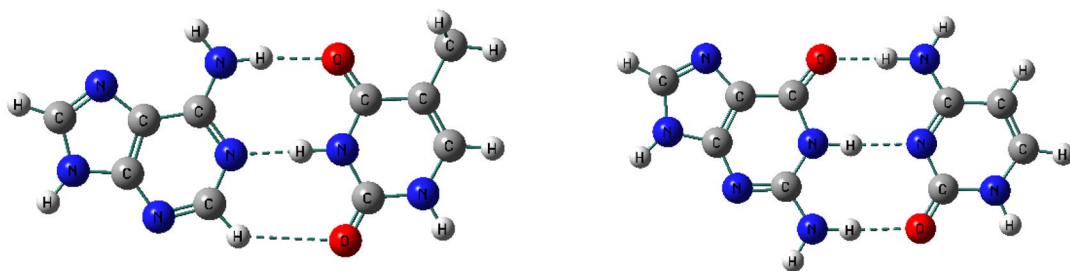


Figure 3: Base pairs adenine–thymine (left) and cytosine–guanine (right) are widely considered to be bound by 2 and 3 ‘conventional’ hydrogen bonds, respectively. A third C–H...O hydrogen bond in AT base pair has been discussed sparsely.

We had built a pulsed nozzle Fourier transform microwave spectrometer¹⁴ to investigate weakly bound molecular complexes. These were generally classified as van der Waals complexes or hydrogen-bonded complexes. Klemperer et al.¹⁵ had used a molecular beam electric resonance spectrometer and solved the structure of $C_2H_4-H_2O$ complex which had the O–H pointing towards the π electrons in C_2H_4 forming an O–H... π hydrogen bond. The first complex investigated in our group was $C_2H_4-H_2S$ and we found the structure to be similar, having an S–H... π hydrogen bond. Our manuscript reporting this first result was published¹⁶ in *Chemical Physics Letters* following favourable comments from two reviewers. However, one of the reviewer suggested that the complex is not called ‘hydrogen bonded’ and these two words were in the title. We agreed to change the title to Rotational spectra and structure of the floppy $C_2H_4-H_2S$ complex: bridging hydrogen bonding and van der Waals interactions. Referees comment made me curious and I started reading about hydrogen bonding.

At that time, hydrogen bonding was defined by IUPAC¹⁷ as “A form of association between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges. Both electronegative atoms are usually (but not necessarily) from the first row of the Periodic Table, i.e., N, O or F. Hydrogen bonds may be intermolecular or intramolecular. With a few exceptions, usually involving fluorine, the associated energies are less than 20–25 kJ mol⁻¹”. This definition seemed outdated. It not only ignored the definition given in 1960 in the first book on hydrogen bond by Pimentel and McLellan¹⁸ (*wide infra*) but also the voluminous work on C–H...O hydrogen bonds

that was beautifully summarized in another book published in 1999 by Desiraju and Steiner.¹⁹

If one looks at the structure of A–T and C–G base pairs given in Fig. 2, it is easy to identify the hydrogen bonds formed by N–H and O–H groups. As this manuscript was being written, as I stared at the structure of A–T base pair, I was wondering if there is any C–H...O hydrogen bond in the A–T base pair! This question has been discussed in 2012 by Horovitz and Trievel²⁰ and they have concluded that direct experimental probing of C–H...O hydrogen bonding in base pairs would be a promising area of research. It appears that, such an exercise has not been carried out yet.

Somewhat coincidentally, an executive committee from IUPAC was visiting Bangalore in 2004. After some discussion, IUPAC was convinced that the definition given was not accurate and invited me to submit a proposal to come up with a new definition. A task group with 14 members recommended a new definition²¹ as follows: “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”. A technical report was published outlining the rationale behind the new definition.¹⁰ This definition appears to have been well accepted in the literature as one can see from citations received for the IUPAC recommendation (1107 in Google scholar and 786 in Web of Science on 30 November 2019) and technical report (747 in Google Scholar and 555 in Web of Science). However, the IUPAC website and Gold Book still carry the old definition!²²

Latimer and Rodebush start their paper with comments about electronegative and electropositive elements and these terms have been taken from the paper by Lewis. Though, they used

electronegative and electropositive nature of the elements in their discussion on polarity and ionization, their discussion on hydrogen bond focuses exclusively on OH group as a donor. It also appears that they had not thought of NH₃ and HCl as hydrogen bonding molecules among themselves. However, Latimer and Rodebush, refer to some unpublished work by Huggins, in which he ‘has used the idea of a hydrogen kernel held between two atoms as a theory in regard to certain organic compounds’. Huggins refers to his Undergraduate Thesis submitted to the University of Berkeley (which appears to have been lost) in his paper published in 1936:²³ It seemed reasonable that a hydrogen kernel, like the silver kernel in this example, should be able to hold to two sufficiently electronegative atoms in this way: X::X. Such “hydrogen bridges”^{*} were postulated, for instance, between oxygen atoms of oxyacids and between fluorine atoms in polymerized hydrogen fluoride. Huggins preferred ‘hydrogen bridge’ rather than ‘hydrogen bond’ as the ‘hydrogen bond’ may be confused with the covalent bond in H₂. Today, no one would have that confusion, though one cannot rule out the possibility that the search in the web of science could include papers discussing hydrogen ‘bonded’ to any atom.

Not only Huggins, but also Pauling,² who made hydrogen bonds more popular by including a chapter in his book focusing on it, emphasized electronegativity. In his book, Pauling states: “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”. It is now recognized that the hydrogen bond is largely ionic in character, and that it is formed only between the most electronegative atoms. Pauling has been hugely influential and this statement led to unnecessary arguments and controversies about hydrogen bonds formed by C–H groups in particular. His influence can be best summarized in the discussion by Badger and Bauer²⁴ in 1937, who were the first to point out that X–H stretching frequency is red-shifted following X–H...Y hydrogen bond formation. In their words: “Recently, there has been considerable interest shown in a peculiar form of linkage sometimes known as the “hydrogen bond” in which a hydrogen atom, usually belonging to an hydroxyl or amino group, appears to serve as a connecting bridge between two electronegative atoms. To establish such criteria (given above) one must of course decide what is meant by a hydrogen bond. Shall the term be reserved for certain cases in which O–O or other internuclear

distance concerned and energy required to break the bond lie within rather narrow limits, or shall it be extended to include a great variety of weaker interactions such as are responsible for the low frequency of vibration of the O–H group in single molecules of the acids and in ortho-chlorophenol, and for a part of the heats of vaporization of HCN and HCl? These latter, of course, merge into the group of interactions known as van der Waals forces”. As mentioned in Sect. 1, any time there was some confusion about a specific interaction, most authors had concluded that it could be *van der Waals*.

The IUPAC technical report¹⁰ discusses the various groups that can form hydrogen bonds and does not limit the atoms to the most electronegative elements. Kumler discussed C–H...N hydrogen bonds in 1936²⁵ and Rao and Jatkar²⁶ discussed ‘Evidence for H bond in benzene’ in 1943 in this Journal. Clearly, Pimentel and McClellan,¹⁷ who wrote the first book on hydrogen bond were aware of these and proposed a definition as follows: “A hydrogen bond is said to exist when: (1) there is evidence of a bond 2) there is evidence that this bond specifically involves a hydrogen atom already bonded to another atom”. One can see the influence of this definition in the IUPAC definition from 2011, except for the insistence that H be bonded to a more electronegative element. However, it appears that Pauling still had great influence and there was a huge opposition to anyone and everyone who dared to mention C–H...O hydrogen bond. Dorothy June Sutor dared to publish an article in 1962 highlighting the importance of C–H...O hydrogen bond.²⁷ A recent article²⁸ in *Chemistry World* describes the struggle she went through. However, the opposition was so strong that Desiraju and Steiner¹⁹ ended up titling their classical book, *The Weak Hydrogen Bond*. The definition they proposed in their book: The weak hydrogen bond may be defined as an interaction X–H...A, wherein a hydrogen atom forms a bond between two structural moieties X and A, of which one or even both are only of moderate or low electronegativity.

The dogma that X and Y must be more electronegative has led to authors coining more names or grouping some interactions as *van der Waals*, rather arbitrarily. For example, Crabtree et al.²⁹ introduced ‘*dihydrogen bond*’, as a new type of intermolecular interaction, the H...H or *dihydrogen bond*, which operates between a conventional hydrogen bond donor such as an NH or OH bond as the weak acid component and an element–hydride bond as the weak base component,

where the element in question can be a transition metal or boron. Clearly, an H atom bonded to the less electronegative B would be hydridic in nature and Crabtree et al. realized that it could accept a hydrogen bond. Grabowski et al.³⁰ while discussing the ‘dihydrogen bond’ and ‘X–H...H₂ interaction’ concluded as follows: “A complete analysis (AIM, energy decomposition, CBS limit...) of the different parameters of the complexes shows that the stronger complexes (dihydrogen bonded) may be classified as H bonded and the weaker complexes (X–H...H₂) may be classified as van der Waals”. Munshi and Guru Row, while comparing C–H...O and C–H... π interactions concluded the following³¹: “Based on the set of criteria defined using the AIM theory it has become possible to distinguish between a hydrogen bond (C–H...O) and van der Waals interaction (C–H... π)”.

The general definition given by Pimentel and McLellan does not put any restriction on electronegativity and according to it, diborane would have two hydrogen bonds and the recent IUPAC definition excludes this. This exclusion is needed as a convention to avoid different terminologies as best illustrated by the Lewis dot structure for H₂O–H₂O, as shown in Fig. 1. This is not oxygen bond but a hydrogen bond. Today, O and other Group 16 atoms could be involved in intermolecular bonds as electrophiles and these have been called *chalcogen bonds*.³² It has been recognized that all the main group elements, from Group 13 to 17, could have similar ‘intermolecular bonds’ and they have been named halogen bonding,³³ chalcogen bonding³², pnictogen bonding³⁴, carbon bonding³⁵/tetrel bonding,^{36,37} and triel bonding.³⁸ About the alkali and alkaline earth group, lithium bonding,³⁹ beryllium bonding,⁴⁰ and magnesium bonding^{41,42} have all been proposed. We propose the term ‘alkalene bonding’ to cover all intermolecular bonds formed by alkali and alkaline earth group.⁴³ That hydrogen bonding cannot be grouped with lithium bonding would not be contested by anyone. Should we have unique names for any other elements? As someone who proposed carbon bonding, I am convinced that this terminology is important and grouping with other Group 14 elements would miss out the significant difference between C and other group 14 elements. Our recent work on protonated methane/silane/germane highlight this aspect.⁴⁴

In fact all the six points mentioned in the Cover graphics were considered sacrosanct and have led various scientists coming up with names and criteria that turned out to be arbitrary. Klemperer et al. named HF...ClF complex⁴⁵ as ‘anti-hydrogen bond’ as they expected it to

be hydrogen-bonded ClF...HF initially. Now we know this to be an early example of a halogen bonded complex. Hobza et al. called some hydrogen bonds as anti-hydrogen bond, if they displayed a blue-shift in stretching frequency rather than the well-known red-shift.⁴⁶ They then changed the name to ‘improper hydrogen bonds’.⁴⁷ Jorly and Jemmis⁴⁸ showed that there is nothing anti- or improper about these hydrogen bonds and there could be red-, blue- or zero-shift hydrogen bonds. Klein and Weinhold⁴⁹ called the hydrogen bond between F[–] and HCO₃[–] ‘anti-electrostatic hydrogen bond’, though there was nothing anti-electrostatic about it. It is indeed a classical charge–dipole interaction leading to hydrogen bond formation in this case. In fact, it was pointed out earlier by Alkorta et al. who titled their paper as ‘Electrostatic origin of the hydrogen bond between anions’.⁵⁰

From the early days of hydrogen bonding, there have been a debate about electrostatics vs covalency and the IUPAC technical report¹⁰ does discuss this in detail. It points out that no single physical/chemical force can be attributed to hydrogen bonding. Just recently, we did a relook on homonuclear diatomic molecules involving all Period 2 atoms,⁵¹ from Li to Ne and showed that they display all the diversity one can find in intermolecular bonding one encounters in chemistry and biology. It would have been appropriate to close this article by quoting Buckingham, who was an earlier champion of the ‘electrostatics in hydrogen bond’.⁵² He had published a paper⁵³ in 2008 titled Hydrogen bonding, and he says the following: “the debate about the origin of hydrogen bonding is relegated to history’ following the universal acceptance of quantum–mechanical nature of all interactions”. However, the history of hydrogen bond and the subjective nature of classifying the interactions/bonds, makes me wonder if the discussion on the nature and criteria for a hydrogen bond would continue in future. For example, Quinn et al.⁵⁴ had analysed the C–H...O contact in AT base pair and found a bond critical point for the same and according to Bader⁵⁵ that would have been a hydrogen bond. However, they concluded that the C–H...O contact represents van der Waals interaction. This conclusion was already made in the book¹⁹ by Desiraju and Steiner. On the contrary, according to the widely followed criteria given by Koch and Popelier⁵⁶ for C–H...O contact, it is a hydrogen bond! Ramachandran and Sasisekharan pointed out the importance of C–H...O hydrogen bonds in the triple-helix structure of collagen⁵⁷. Hydrogen bonding and indeed, the discussion about it, has no borders.⁵⁸

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