Interatomic Distances in Hydrogen Bonds from Molecular Tensegrity: Atomic Sizes as Descriptor.

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Abstract.

Molecules are treated as tensegrity structures and a molecular tensegrity is defined to obtain quantitative information on 1,3- distances in X-M-Y linkages. We apply these principles to A···H-B hydrogen bond complexes. In this approach a tensegrity factor is obtained from the ratio of ideal A···H or H-B distances to that of ideal A···B distances from sizes, $CR_0^{\pm}$, that are associated with positive and negative sizes of atoms and which are obtained as fixed functions of atomic size, r_{nZ}^{c}. Limiting values of various A···B distances for “n-polar” (ionic) and “neutral” sizes are obtained for coordination number, $N = 4$ or 6 without requiring a knowledge of the actual positions of the hydrogen atom. In this formulation the A···B distance decreases with increasing N. The calculated distances with $N = 4$ are closer to most observed A···B distances in A···H-B hydrogen complexes in (> 1000) compounds of biologically important amino acids. The shorter O···H-O and O···H-N hydrogen bonds are consistent with “n-polar” distances ($N = 4$). Others, including O···H-C or C···H-O are better characterized by the longer “neutral” distances. Very short hydrogen bonds (SSHBs or LBHBs) correspond to distances calculated with $N = 6$. The way the molecular tensegrity of the A···H-B hydrogen bond complexes impacts the length of A···H and H-B bonds are discussed.

1. Introduction

A tentative IUPAC definition [1, 2] for an A$\cdots$H-B hydrogen bond complex is that there should be an attractive interaction between a B-H group in a molecule and an atom (or group of atoms) Y in the same or another molecule. An important descriptor in theoretical studies of hydrogen bonding has been the strength of the binding energy of the hydrogen bond complex. However, as emphasized by Buckingham *et al* [1], a wide range of interactions contribute to the binding energies so that one would require various qualifying descriptions of the hydrogen bond and terminologies such as the *normal* hydrogen bond between neutral molecules. The vibrational frequency of the B-H bond in the normal A$\cdots$H-B complex is normally red-shifted [3] on the formation of the complex. The proton NMR chemical shift in normal hydrogen bond complex is downfield (usually < 5 ppm) which may be interpreted as having less electron density around the hydrogen on the formation of the complex. Exceptions to the *normal* hydrogen bond are thus those with blue-shifted B-H vibrations, or with very large downfield proton NMR chemical shifts besides those which are proton-shared [4]. Our interest in this submission is somewhat different. We intend characterizing hydrogen bond A$\cdots$H-B complexes through the interatomic separations in the complex. Thus there could be normal and short or long interatomic distances.

There is a fickle-ness in the literature in identifying the actual pair of atoms in the A$\cdots$H-B complex which are to be evaluated by their interatomic separations. It has been the conventional wisdom that the proton in the hydrogen bond is buried in the electron cloud of the B atom in an A$\cdots$H-B linkage such that the hydrogen bond contacts are just the sum of van der Waals' radii of A and B atoms. The van der Waals' sizes, r_{vdW}, of atoms have been used [3] to characterize hydrogen bond distances although tabulated values [3, 4] of these radii may differ considerably. The formation of a hydrogen bond is also usually indicated when the A$\cdots$H distance is smaller than the sum of the van der Waals' radii of the A and H atom. Such a shortening of the distance has been attributed [4] to the formation of three-centre four-electron bonds with considerable electron overlap between the orbitals of A, H and B atoms. Our approach will not consider consequences of variable electron overlap.

Our focus will be mainly on the A$\cdots$B distances. Of recent biological interest are the so-called short strong hydrogen bonds (SSHBs) (5-7]. By its very name, the identification of SSHBs is based on the shorter A$\cdots$B separations (by about 20-40 pm) as compared to the separations in the normal hydrogen bond. It is proposed that the transition state is stabilized because of the short A$\cdots$B distance and that the barrier between two possible A$\cdots$H-B or A-H$\cdots$B hydrogen bonded complexes is lowered. The SSHBs are sometimes taken to be synonomous [5-7] with low-barrier hydrogen bonds (LBHBs), and are characterized by large downfield proton chemical shifts (typically 20 ppm). The large downfield proton NMR shift in SSHBs is taken as measure of increasing proton-like acidity of the hydrogen atom that would account for the short O$\cdots$O distance in SSHBs as in proton-shared hydrogen bonds such as those in $(O_2H_5)^+$ [O$\cdots$O distance ~ 238 pm; see Ref 1]. However, theoretical calculations on binding energies and chemical shifts by Del Bene *et al* [4] on a number of hydrogen-bonded complexes reveal that proton-shared hydrogen bonds have NMR shifts of ~ 20 ppm without being dependent on the binding energy.

The geometries of hydrogen-bonded A···H-B complexes in terms of ^{1}H NMR parameters may be understood in terms of Pauling's valence bond order or bond valences [8-12]. A recurring theme in A···H-B hydrogen bond complexes is that a decrease in bond order of the B-H bond on complex formation is accompanied by an increase in bond order of the A···H bond with the total bond order being unity. In chemical terms this implies that in the normal hydrogen bond complexes the covalence of the B-H bond decreases while that of the A···H "non-bond" increases as the A···B distance decreases. A measure of the "overlap of electron clouds" or "covalent" nature of a B-H bond is obtained from the spin-spin coupling between two atoms [13]. The theoretically evaluated reduced one-bond B-H coupling constants, $^{1}J_{B\text{-}H}$, for B-H monomers as well A···H-B hydrogen bond complexes show little correlation with B-H distances [14]. However, $^{1}J_{B\text{-}H}$ for different B in complexes with C-H, N-H, O-H, and FH have been related [14] for the first time through the normalized changes in $^{1}J_{B\text{-}H}$ and changes in B-H distance on complex formation from the monomeric state as well as the square of the Pauling electronegativity difference between the B and H atoms.

The theoretically evaluated [14] two-bond spin-spin coupling constants, $^{2h}J_{A\text{---}B}$ across A···H-B hydrogen-bonded complexes ("2h" indicates that the coupling is across the two A···H and H-B bonds) show a single-curve correlation between $^{2h}J_{A\text{---}B}$ and the distance $d_{A\text{---}B}$ between the A and B atoms for N-H-N and C-H-N systems. Such a correlation holds even though the complexes could be neutral or charged implying different levels of hybridization in bonds involving the hydrogen atom. The seeming contradiction pointed out [14] in such a correlation is that $^{2h}J_{N\text{-}N}$ term would seem to be independent of the nature of the N-H hybridization although hybridization is considered to be important in accounting for changes in B-H distances. Although the hydrogen bond complex A···H-B implies changes due to the contact of hydrogen in the B-H bond with an atom A the nature of these contacts need not directly correlate with the A···B separation. This is an important aspect that we require considering.

It is pertinent to note from a historical point of view, the first description of hydrogen bonding [15] stressed the importance of the high dielectric constants of hydrogen bonded systems. This has been attributed to proton displacements from the centre of the atom. An important consequence of such atomic displacements in Latimer's model—or as a consequence of asymmetric bonding effects in modern theoretical approaches—is that the spherical atom approximation is no longer valid. This poses considerable difficulty [16] in locating the hydrogen atom from electron densities obtained from X-ray diffraction studies since the hydrogen has no core electron to identify it by. This ambiguity in locating the hydrogen atom is inevitable and unavoidable. In neutron diffraction studies the position of the nucleus is more accurately determined as the nuclear position may be accurately represented as a point-scatterer. On the other hand, since electron densities are to be related to chemical reactivity, one may be actually interested in the electron density profiles obtained by X-ray refinements. The discrepancies between X-ray and neutron diffraction results affect the way the non-bonded A···H distance is to be evaluated. The

A···B distance is more reliably obtained experimentally and one requires a method for evaluating these distances without specifically requiring to know the A···H or B-H distances, at least to a first approximation.

Buckingham *et al* [1] have considered the internuclear A···B distance as one of three experimentally measured quantity that requires reliable theoretical interpretation without necessarily accounting simultaneously for changes in distances involving the hydrogen atom in the complex. In this submission we examine the values of expected A···B distance in A···H-B hydrogen bond complexes from considerations of molecular tensegrity even if this theoretical model may be different from that conventionally used. The concept of molecular tensegrity has been used earlier [17-19] for obtaining 1,3- non-bonded distance in X-M-X' linkages in gas-phase MX_n compounds. In this approach (see section 2.3), the ideal 1,3-X···X' distances are obtained from a knowledge of "ideal" "charge-transfer" single-bond M-X distances, $d^{00\pm}$, and a size, $CR_0^-(X)$, of the X atom, which are themselves simple linear function [20] of atom-specific sizes [20-22], r_{nZ}^c. There is no requirement for knowing the actual M-X or M-X' distances. We apply these concepts to the A···H-B hydrogen bonded complexes since we would not require accurate knowledge of A···H or B-H distances.

We emphasize, in particular, the way the "ionic" (or "*n*-polar") sizes [20, 21], CR^-, and the "neutral" (or what is loosely identified with vdW size, r_{vdW}) sizes may be used to obtain cut-off limits for the A···B distances in strong and weak hydrogen bonds in A···H-B complexes. We ignore other debates [2, 23-25] on the way the interatomic A···B van der Waals contact distances should be compared by taking into account the AHB bond angle. The van der Waals dispersion reaction interaction between atoms is a consequence mainly of the induced-dipole induced-dipole interactions between atoms. It is expected to be isotropic, to first order so that the magnitude of the A···B van der Waals interaction in the A···H-B hydrogen bond complex may have little dependence on the AHB angle.

In what follows we describe first in sec 2 the way we obtain [20-22] atomic sizes and interatomic distances (details of which are given in the Appendix for those interested) and the concepts used for obtaining 1,3-distances in X-M-X' linkages in a molecular tensegrity model [17-19]. In sec 3 we extend the molecular tensegrity model to calculate "1,3-" A···B distances in A···H-B hydrogen bond complexes. In this calculation there is no requirement for knowing the actual A···H or H-B distances with a provision being made for the "polar" or "neutral" nature of the contacts and the number, *N*, of contacts the hydrogen atom has with other atoms outside the A···H-B complex. In sec 4 we compare the calculated distances with observed A···B distances for A···H-B compounds in general. In sec 5 we examine the short A···B distance in LBHBs in the context of hydrogen-sharing between A and B atoms and increase in the nominal value of *N*, when there are furcated hydrogen bonds. In section 6 we consider briefly the A···H-B hydrogen bond complexes in which neither A nor B are O or N. In section 7 we illustrate the effect of electronegativity difference between A and B atoms in A···H-B and B···H-A hydrogen bond complexes with special emphasis on C···H-O hydrogen bonds and O···H-C hydrogen bonds. Finally in sec 8 we show the linear dependence of A···H distance and the A···B distance and a hint of a possible exponential decay of the H-B distance with increase in A···H distance.

2. Atomic Sizes, Interatomic Distances and Molecular Tensegrity

2.1. Atomic Sizes.

The atomic sizes, r_{nZ}^{c}, used by us have been obtained from a classical stationary point in a new model [20-22] and without adjustable parameters. The basic premise of this model is that atomic sizes are defined by external interaction which is represented by the absorption or emission of a photon—or a virtual photon in vacuum—which, in turn, is represented by an electron-hole pair, (e^{-}-h^{+}). The atomic size is obtained [20-22] by considering the interaction of the outer-electrons with the hole, h^{+}, of the electron-hole pair that represents the external interaction. Because h^{+} is a universal component of the external interaction field, ($e^{-}h^{+}$), the atomic size thus obtained is not dependent on the actual nature of the external interaction. It is, however, atom-specific, because it is dependent on the way the outer electrons are distributed, say, between the valence and inner shells, as well as the way the *d*- and *f*- electrons of transition metal elements are treated. This is the new paradigm shift in which an external field is used to define an atomic size instead of calculating the size of an isolated atom internally. Some of the sizes of atoms that we will be using in this submission are given in Table 1 (note that the sizes are in atomic units).

For a given bonding or non-bonding interaction the interatomic distance is given [20] as the sum of a size, *CR*, which is a linear function of the size r_{nZ}^{c} of the atom involved with

$$CR = Cr_{nZ}^{c} + D \qquad (1)$$

The coefficient *C* in eqn 1 is atom-independent coefficient for the given interatomic interaction and the constant *D* is the size of the hydrogen atom for the given interaction.

2.2. 1,2-Interatomic Bonded Distances.

A general expression [20] for interatomic distances, $d_{M\text{-}X}$, for an M-X bond is written (for convenience), in terms of a "hub" and "axle" description with

$$d_{MX}(\text{cal}) = \varepsilon_{\text{eff}}[\{C_M r_{nZ}^{c}(\text{M})/F_S(\text{M}) + C_X r_{nZ}^{c}(\text{X})/F_S(\text{X})\}_{\text{"hub"}} + \{D_M/F_S(\text{M}) + D_X/F_S(\text{X})\}_{\text{"axle"}}] \qquad (2)$$

The term F_S takes [26, 27] into account the shortening of bond distances due to the presence of n_v "unsaturated" (or what we henceforth term as "extrabonding") electrons. F_S is empirically found [26, 27] to be $F_S = 1.18$, 1.26, 1.32, 1.38 and 1.42 for $n_v = 1$, 2, 3, 4 and 5, respectively. Writing n_v in terms of a spin S_v ($= n_v/2$) valence electrons that contribute [28] to bond order ($= n_v + 1$) we write $F_S \approx [1 + (2/\pi)^2\{S_v(S_v+1)\}^{1/3}$. For this article we will require $F_S = 1$. The values of the coefficients $C_{M,X}$ or $D_{M,X}$ for the "hub" and "axle" sizes for M and X atoms usually correspond to either "charge-transfer" values (see appendix; X is taken to be the more electronegative atom) or "neutral" values ($C = 1, 2, \ldots, D = 1, 2 \ldots$). The "charge-transfer" values are observed for gas-phase compounds in which M and X are both atoms of insulating elements or in solids [20].

In what follows we will require an "ideal" ($\varepsilon_{\text{eff}} = 1$ in eqn 2) "single bond" ($F_S = 1$ in eqn 2) "charge-transfer" distance, $d^{00\pm}$, for the non-transition metal elements we study in this paper. This “ideal” M-X (r_{nZ}^{c}(M) ≥ r_{nZ}^{c}(X)) charge-transfer distance is a single-bond distance for $\varepsilon_{\mathrm{eff}} = 1$ and is given by

$$d_{MX}^{00\pm} \equiv CR_0^{+}(\mathrm{M}) + CR_0^{-}(\mathrm{X}) \tag{3a}$$

with

$$CR_0^{\pm} \equiv C_0^{\pm} r_{nZ}^{c} + D_0^{\pm} \tag{3b}$$

with $C_0^{+} = 2.144$, $C_0^{-} = 2.30$, $D_0^{+} = -2a_H/3$ and $D_0^{-} = 2a_H$ (see appendix for a possible derivation of for the values of $C_0^{\pm}$ in eqns A4 and A5). We thus obtain the “ideal” distance as

$$d_{MX}^{00\pm} \equiv 2.144 r_{nZ}^{c}(\mathrm{M}) + 2.30 r_{nZ}^{c}(\mathrm{X}) + 4a_H/3 \tag{4}$$

The zeros in the superscript or subscript indicates that there are no “extrabonding” valence electrons or $n_v(\mathrm{M}) = n_v(\mathrm{X}) = 0$ or $F_S(\mathrm{M}) = F_S(\mathrm{X}) = 1$ in eqn 2 as expected for single bonds.

2.3. Molecular Tensegrity and 1,3-Distances.

For an X-M-X linkage, we have used [17-19] “tensegrity factor”, $t^{00\pm}$, as a measure of the matching of idealized “charge-transfer” M-X (eqn 3) and X- - -X distances. The“ideal” charge-transfer separation, $d_{XX}^{00=}$, between the X atoms in the X-M-X linkage is obtained from eqn 2b as

$$d_{XX}^{00=} = 2CR_0^{-}(\mathrm{X}) = 2(2.300 r_{nZ}^{c}(\mathrm{X}) + 2a_H) \tag{5}$$

From these considerations, the tensegrity factor, $t_{MX}^{00\pm}$ is obtained as

$$t_{MX}^{\ 00\pm} = d_{MX}^{00\pm}/d_{XX}^{00=} \approx 0.5[CR_0^{+}(\mathrm{M})/CR_0^{-}(\mathrm{X}) + 1] \tag{6}$$

In the way eqns 1 – 5 are written, $t_{00}^{\pm}$ is dependent only on the core atomic size, r_{nZ}^{c}, of M and X atoms without requiring separate estimates of ionic character, for example.

One appealing feature of eqn 6 is that the tensegrity factor, $t^{00\pm}$, is dependent on the ratio $\mathrm{R}^{\pm} = CR_0^{+}(\mathrm{M})/CR_0^{-}(\mathrm{X})$, which is the radius ratio of the charge-transfer sizes of M and X atoms. It is well known that there are geometrical limits to the value of $\mathrm{R}^{\pm}$ for various coorination numbers, N. One can then expect the tensegrity factor to depend on the coordination number, N. One then obtains limiting values, $t^{00\pm}_{\lim\to N}$ for limiting values of the ratio $\mathrm{R}^{\pm}$ [19-23] for the regular octahedron and the tetrahedron which, other than the icosahedron, are the fundamental polyhedra for describing tensegrity structures [29]. For example, for $N = 4$ (tetrahedron) and $N = 6$ (octahedron) the upper limiting values of $\mathrm{R}^{\pm}$ are 0.414 and 0.732, respectively. Thus, $t^{00\pm}_{\lim\to N} = 0.707$ and 0.866 for $N = 4$ and 6, respectively.

The changes in the X$\cdots$Y distance in X-M-Y linkages is given by a coordination-number-dependent or N-dependent term F_S^{*N} in the molecular tensegrity approach. This term, given by

$$F_S^{*N} = [2 - t^{00\pm}/t^{00\pm}_{\lim\to N}] \tag{7}$$

is now introduced as a measure of the matching of the 1,2- M-X and the 1,3- X$\cdots$X distances with $F_S^{*N} = 1$ when $t^{00\pm}/t^{00\pm}_{\lim\to N} = 1$. The N-dependence comes through the term $t^{00\pm}_{\lim\to N}$ in eqn 7. The X$\cdots$X distance for gas-phase MX_n compound may be written in terms of a size CR(X) as

$$d_{X\text{---}X}^{\ 1,3} = 2CR(\mathrm{X})^{1,3}/F_S^{*N} \tag{8a}$$

$$= 2\mathrm{K}\varepsilon_{\mathrm{XX}}[2.3 r_{nZ}^{c}(\mathrm{X}) + 2a_H]/\ [2 - t^{00\pm}/t^{00\pm}_{\lim\to N}] \tag{8b}$$

It is seen from eqns 7 and 8 that when $F_S^{*N} > 1$ there is a contractive pressure on the 1,3-X$\cdots$X distance tending to compress it from its ideal value, $2CR_0^-(\mathrm{X})$ or $d_{XX}^{00=}$ (eqn 5). When $F_S^{*N} < 1$ the 1,3-distance would tend to expand over $2CR_0^-(\mathrm{X})$. The size $CR(\mathrm{X}) = \mathrm{K}\varepsilon_{\mathrm{XX}}CR_0^-(\mathrm{X})$. $\mathrm{K} = 1$ or $\mathrm{K} = 1.125$ in eqns 8 correspond [21'] to "n-polar" (or "ionic") and "neutral" (or van der Waals) sizes of the X atom, respectively. The term, ε_{XX}, is an effective dielectric constant which allows for small changes due to environmental influences in a manner consistent with the size of the atom. For the purpose of this communication we use the empirical relationship

$$\varepsilon_{\mathrm{XX}} = 1 + [0.0019\{2(2.3r_{nZ}^{c} + 2a_H)\}]^6 \tag{9}$$

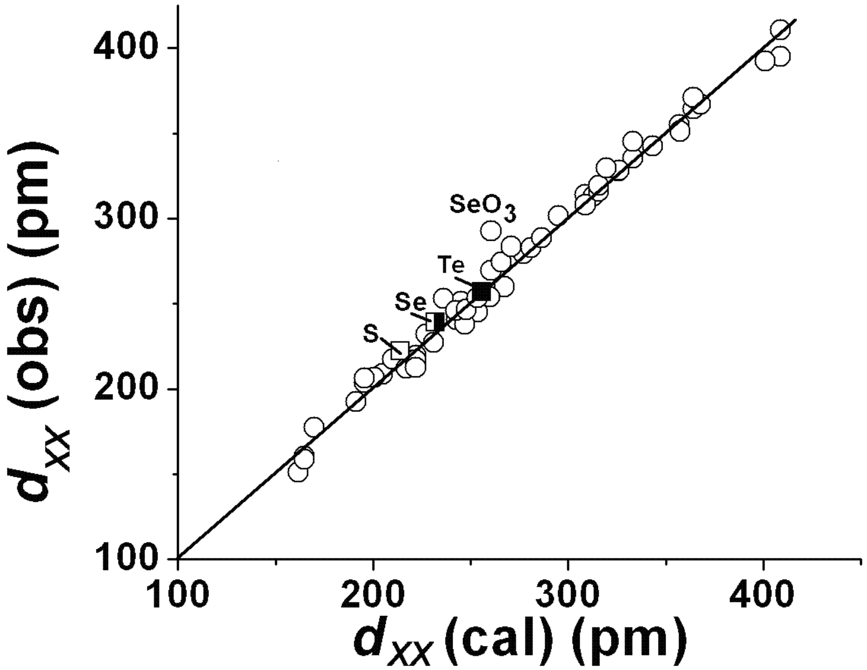

Fig 1. Plots of observed X$\cdots$X distances (from ref 21) in gas-phase MX_n compounds (X and M are atoms of insulating elements) *vs* calculated distances from eqns 6-8 and atomic sizes from Table 1. Circles: $n \le 4$, $N = 4$, $\mathrm{K} = 1$; Squares: $N = 6$, $\mathrm{MF_6}$ compounds ($\mathrm{M = S}$, $\mathrm{K = K_{polar}} = 1$; $\mathrm{M = Se}$, $\mathrm{K = (K_{polar} + K_{neutral})/2} = 1.0625$; $\mathrm{M = Te}$, $\mathrm{K = K_{neutral}} = 1.125$).

For an X-M-Y linkage the X$\cdots$Y distance has been found to be given by

$$d_{X\text{---}X'}^{\;1,3} = \{CR(\mathrm{X}) + CR(\mathrm{Y})\}\,/F_S^{*N} \tag{10a}$$

$$= \mathrm{K_X}\varepsilon_{\mathrm{XX}}\{2.3r_{nZ}^{c}(\mathrm{X}) + 2a_H\}/\{2 - t_{MX}^{00\pm}/t_{MX}^{00\pm}{}_{\lim\to N}\} + \mathrm{K_Y}\varepsilon_{\mathrm{YY}}\{2.3r_{nZ}^{c}(\mathrm{Y}) + 2a_H\}/\{2 - t_{MY}^{00\pm}/t_{MY}^{00\pm}{}_{\lim\to N}\} \tag{10b}$$

The provision is made that $\mathrm{K_X}$ need not be the same as $\mathrm{K_Y}$ and could have as before $\mathrm{K = K_{polar}} = 1.00$ or $\mathrm{K = K_{neutral}} = 1.125$ for "n-polar" or "neutral" distances.

For gas-phase MX_n compounds ($n \le 4$) where M and X are atoms of insulating elements (except $\mathrm{SiH_4}$, $\mathrm{GeH_4}$ and $\mathrm{KrF_2}$ and $\mathrm{XeF_2}$) we find [22] that $\mathrm{K} = 1$ and $\mathrm{N} = 4$, gives the 1,3-X$\cdots$X distances satisfactorily as shown in Fig 1. For $\mathrm{MX_6}$ compounds ($n = 6$) the calculated values are too large when we use $N = 4$ in eqns 7 and 8, even with $\mathrm{K} = 1 = \varepsilon_{\mathrm{XX}}$. Good fits are obtained only when we use $N = 6$ and allow for variations in K (see fig 1 for

MF_6 compounds; M = S, Se, Te). This highlights the way an increase in coordination number could lead to a decrease in the 1,3- distances. We shall use this aspect for understanding short hydrogen bond lengths [5-7] in LBHBs (or SSHBs).

3. Calculated A···B Distances in Hydrogen-Bonded AHB Hydrogen Bond Complexes.

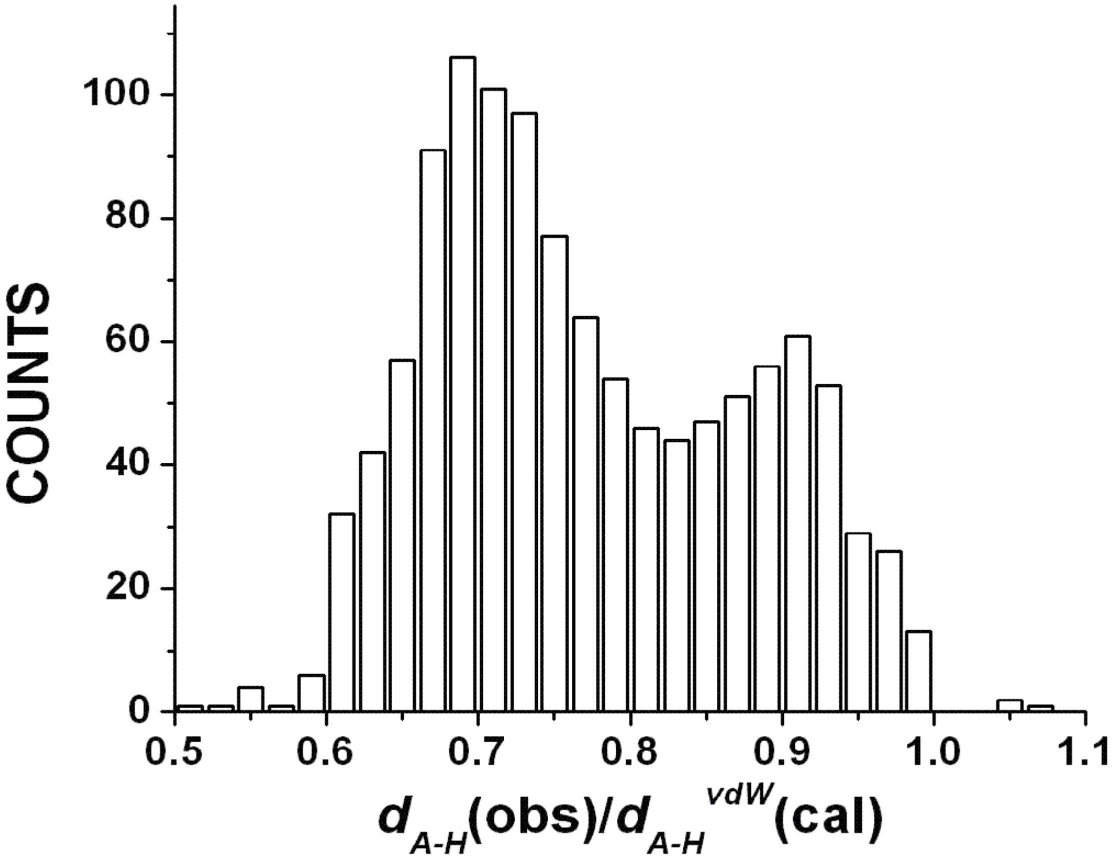

Fig 2. Histograms of number of A···H distances normalized by the sum {= 1.125(CR_0^-(A) + $4a_H$)} of the "neutral" (identified with vdW) sizes of A and H atoms for the compounds studied in this investigation.

A point of detailed interest in this communication is to examine the A···B distance as a 1,3-distance in a A···H-B hydrogen bond complex in terms of the molecular tensegrity model borrowed from Buckminster Fuller's analysis of engineering tensile integrity structures. For the purpose of this communication we have chosen hydrogen bond complexes in compounds of biologically important α-amino acids. We have chosen all A···H-B complexes in which the A···H distance is less than the sum of their "neutral" sizes CR(X) = KCR_0^-(X) distances with K = 1.125. We have normalized the reported A···H distances, d_{A---H} by dividing by of the sum of the "neutral" (K = 1.125) sizes of A and H atoms. The histograms of the ratio $_{A---H}$ obtained from the d_{A---H} distances obtained from CCDC tables for O···H-O, O···H-N and other A···H-B complexes used in this study are shown in Fig 2. It is seen that in all these systems the A···H distances are less than the sum of their "neutral" sizes.

We treat the $A^{\cdots}H\text{-}B$ complex as similar to the X-M-Y linkage and apply equations similar to those in eqn 9. The "ideal" non-bonded $A^{\cdots}H$ distance in the "charge-transfer" model are taken as the sum of the "n-polar" sizes of A and H atoms. We then write (in pm)

$$d_{A\text{- - -}H}^{\;00=} = CR_0^{-}(\mathrm{A}) \; + CR_0^{-}(\mathrm{H}) \equiv CR_0^{-}(\mathrm{A}) \; + D_0^{-}(\mathrm{H}) \qquad (11)$$

$$= (2.30 r_{nZ}^{\;c} + 2a_H) \; + 2a_H \qquad (12)$$

The tensegrity factor, $t^{00=}$, for the $A^{\cdots}H$ component is then that of a hypothetical $A^{\cdots}H^{\cdots}A$ linkage. The = sign in the superscript of eqn 11 indicates that the ideal $A^{\cdots}H$ distance is the sum of "n-polar" sizes of the A and H atoms. The value of $t_{A\text{---}H}^{\;00=}$ is written as

$$t_{A\text{- - -}H}^{\;00=} = \; d_{A\text{- - -}H}^{\;00=}/2CR_0^{-}(\mathrm{A}) \qquad (13)$$

The tensegrity factor $t_{H\text{-}B}^{\;00\pm}$ is obtained in the usual way from eqn 5 as

$$t_{H\text{-}B}^{\;00\pm} = d_{B\text{-}H}^{\;00\pm}/2CR_0^{-}(\mathrm{B}) \qquad (14a)$$

$$= (2.\,144 r_{nZ}^{\;c}(\mathrm{B}) + 70.6)/(2.3 r_{nZ}^{\;c}(\mathrm{B}) + 105.8) \text{ (in pm)} \qquad (14b)$$

The $A^{\cdots}B$ distance is then obtained in a manner similar to that from eqn 9 as

$$d_{A\text{---}B} \; = \; \mathrm{K_A}\varepsilon_{\mathrm{AA}}\{2.3 r_{nZ}^{\;c}(\mathrm{A}) + 105.8\}/\{2 - t_{A\text{---}H}^{\;00=}/t_{A\text{---}H}^{\;00=}{}_{\lim\rightarrow N}\} \qquad +$$

$$\mathrm{K_B}\varepsilon_{\mathrm{BB}}\{2.3 r_{nZ}^{\;c}(\mathrm{B}) + 2a_H\}/\{2 - t_{B\text{-}H}^{\;00\pm}/t_{B\text{-}H}^{\;00\pm}{}_{\lim\rightarrow N}\} \qquad (15)$$

The $A^{\cdots}B$ distance for an $A^{\cdots}H\text{-}B$ hydrogen bond complex can then be calculated (see Table 2) from eqn 15 using the atomic sizes, $r_{nZ}^{\;c}$ some of which are given in Table 1, for a given value of K and values of $\varepsilon_{\mathrm{XX}}$ from eqn 9.

The $F^{\cdots}F$ distance in $(HF)_2$ of ~ 279 pm (see ref 1) agrees with the "normal" (N = 4, K = 1) distance of ~ 281 pm when $\varepsilon_{\mathrm{FF}}$ is calculated from eqn 15. The $O^{\cdots}O$ distance of ~ 298 pm (see ref 1) in water dimer, $(H_2O)_2$, is close to the calculated distance (~ 303 pm, $\varepsilon_{\mathrm{OO}}$ calculated from eqn 15) using N = 4 and average of K = 1 and K = 1.125. The $O^{\cdots}O$ distance of ~238 pm in the $(H_5O_2)^+$ complex is closer to the calculated K = 1, N = 6 value of ~ 236 pm. However, as we shall see later this distance may as well be related to aspects associated with LBHBs (see sec 5, Fig 8). $(H_5O_2)^+$ has been described (see ref 1) as a proton-shared complex with the O—H distance of ~ 119 pm being considerably longer than the distance (97 ± 1 pm) in H_2O or $(H_3O)^+$.

We may calculate the tensegrity factor for a hydrogen-atom-shared hydrogen bond complex which we write as $A\overset{\cdots}{-}H\overset{\cdots}{-}B$ hydrogen bond complex. Such complexes would be typical of LBHBs with the bond order of the $A\overset{\cdots}{-}H$ and $B\overset{\cdots}{-}H$ bond being 0.5 [7, 10] In this case the ideal values of the $A\overset{\cdots}{-}H$ distance, $d_{AH}^{\;<av>}$, is the average of $d_{A\text{---}H}^{\;00=}$ (eqn 12) and $d_{A\text{-}H}^{\;00\pm}$ obtained from eqn 4. Thus, we may write

$$d_{AH}^{\;,< av>} = \; [\{(2.30 r_{nZ}^{\;c} + 2a_H) \; + 2a_H \}+ \{2.144 r_{nZ}^{\;c}(\mathrm{A}) + 4a_H/3\}]/2 \qquad (16a)$$

with

$$t_{AH}^{\;<av>}= d_{AH}^{\;<\mathrm{av}>}/2CR_0^{-}(\mathrm{A}) \qquad (16b)$$

We may similarly write eqns for $d_{BH}^{\;<av>}$ and $t_{BH}^{\;<av>}$ for the $B\overset{\cdots}{-}H$ bond from eqns 16. From considerations similar to that in eqn (15) we then obtain the $A^{\cdots}B$ distance, $d_{A\text{---}B}^{\;<av>}$, in a proton-shared $A\overset{\cdots}{-}H\overset{\cdots}{-}B$ complex as

$$d_{A\text{---}B}^{\;<av>} \; = \; \mathrm{K_A}\varepsilon_{\mathrm{AA}}\{2.3 r_{nZ}^{\;c}(\mathrm{A}) + 105.8\}/\{2 - t_{AH}^{\;<av>}/t_{A\text{---}H}^{\;,00\pm}{}_{\lim\rightarrow N}\} \qquad +$$

$$\mathrm{K_B}\varepsilon_{\mathrm{BB}}\{2.3 r_{nZ}^{\;c}(\mathrm{B}) + 2a_H\}/\{2 - t_{BH}^{\;<av>}/t_{B\text{-}H}^{\;00\pm}{}_{\lim\rightarrow N}\} \qquad (17)$$

In the general case when the hydrogen atom is not equally shared between A and B atoms we may write eqn 16a as

$d_{AH}{'}^{<av>} = [(p)\{(2.30r_{nZ}{}^{c}(\mathrm{A}) + 2a_H) + 2a_H\} + (1-p)\{2.144r_{nZ}{}^{c}(\mathrm{A}) + 4a_H/3\}]$ (16c)

and

$d_{BH}{'}^{<av>} = [(1-q)\{(2.30r_{nZ}{}^{c}(\mathrm{B}) + 2a_H) + 2a_H\} + q\{2.144r_{nZ}{}^{c}(\mathrm{B}) + 4a_H/3\}]$ (16d)

The A$^{\cdots}$B distances may then be calculated from eqn 17 using eqns 16b and its equivalents. In neutral complexes the condition $p = q$ is required. In normal A$^{\cdots}$H-B hydrogen bond complexes $p = q = 1$. In hydrogen shared complexes the A$^{\cdots}$B distance goes through a minimum when $p = q = 0.5$ as in eqn 16a. When $p < q$, the calculated A$^{\cdots}$B distance is expected to be smaller than the case when $p = q = 0.5$. The O$^{\cdots}$O distance of ~ 238 pm in $(H_5O_2)^+$ is obtained, for example, when p ~ 0.65 and q ~ 1. Howeever, the total bond order of the AHB complex in this case is greater than unity with hydrogen having valence greater than unity. This situation is not uncommon in metal hydrides, although it is yet to find acceptance in the study of hydrogen bond complexes. It could give a new insight into A$^{\cdots}$B distances even if it requires more substantiation from experiments (see sec 5).

We have compared in Table 2, the calculated A$^{\cdots}$B distances for various values of K and N from eqn 11-14 with ε_{XX} calculated from eqn 15. For small atomic sizes (e.g., F, O, N) the A$^{\cdots}$B distance calculated from the tensegrity model with $N = 4$ and K = 1 is close to the sum ($\Sigma_{X = A,B}CR_0{}^{-}(X)$) of the "n-polar" sizes of the A and B atoms (see Table 1) rather than the sum of the "neutral or vdW sizes that was assumed early by Buckingham and coworkers [2]. The calculated N = 4, K = 1 distances of O$^{\cdots}$F, N$^{\cdots}$F, C$^{\cdots}$F and C$^{\cdots}$C are to be comparable with the distances of 266, 280, 305 and 367 pm, respectively, used by Buckingham and Fowler in their classic paper [2] for the A$^{\cdots}$B distances in *normal* hydrogen bond A$^{\cdots}$H-B hydrogen complexes. From the way eqns 11-15 are written one does not expect much change in the calculated distances (without changes in K or N) when A and B are interchanged. The actual changes are within 1% in most cases studied and within 2% for the larger changes.

The point of importance in the molecular tensegrity model is that for a given value of K (K = 1, "n-polar"; K = 1.125, "neutral") the A$^{\cdots}$B distance may be shortened on going from $N = 4$ to $N = 6$, or by forming a "hydrogen-atom-shared" A$\overset{\cdots}{-}$H$\overset{\cdots}{-}$B complex. The shortening of the A$^{\cdots}$B distance for a given N (by nearly 25 pm for $N = 4$) for a proton-shared A$\overset{\cdots}{-}$H$\overset{\cdots}{-}$B is particularly satisfying as it is (at least partly) consistent with observed NMR downfield shifts. Such a shortening is possible in the molecular tensegrity model when there is hydrogen sharing between the A and B atoms. The shortening is a maximum when the hydrogen atom is equally shared between the A and B atoms.

The dependence on coordination number, N, could be important from the point of view of the acidity of the hydrogen atom in the A$^{\cdots}$H-B complex. As a general rule, the strongest influence on acidity of a proton bound to an anion depends [30] on the anion stability. Among the factors contributing to anionic stability are resonance effects, hybridization effects and electronegativity effects. From an orbital-based analysis of Pauling's bond valence rules, Burdett and McLarnan [9] have suggested that when there are two anionic species a more electronegative anion should occupy a site with a lower coordination number. As a corollary, changes in coordination number can change the electronegative nature of, say, an anionic species. Thus a change in coordination number from N = 4 to N = 6 would affect the acidity of the proton. Cleland *et al* [7] on discussing the acylation of chymotrypsin have stressed upon the role of active site being compressed on binding to a specific substrate so as to bring His-57 and Asp-102 close together and enabling the formation of HBLBs. As we shall see below an increase in coordination number would lead to a decrease in the A¨B distance. In what follows we shall evaluate the experimentally observed distances with those calculated in eqns 11-17.

4. Comparison of Observed and Calculated Distances.

4.1. A¨H-B compounds in General.

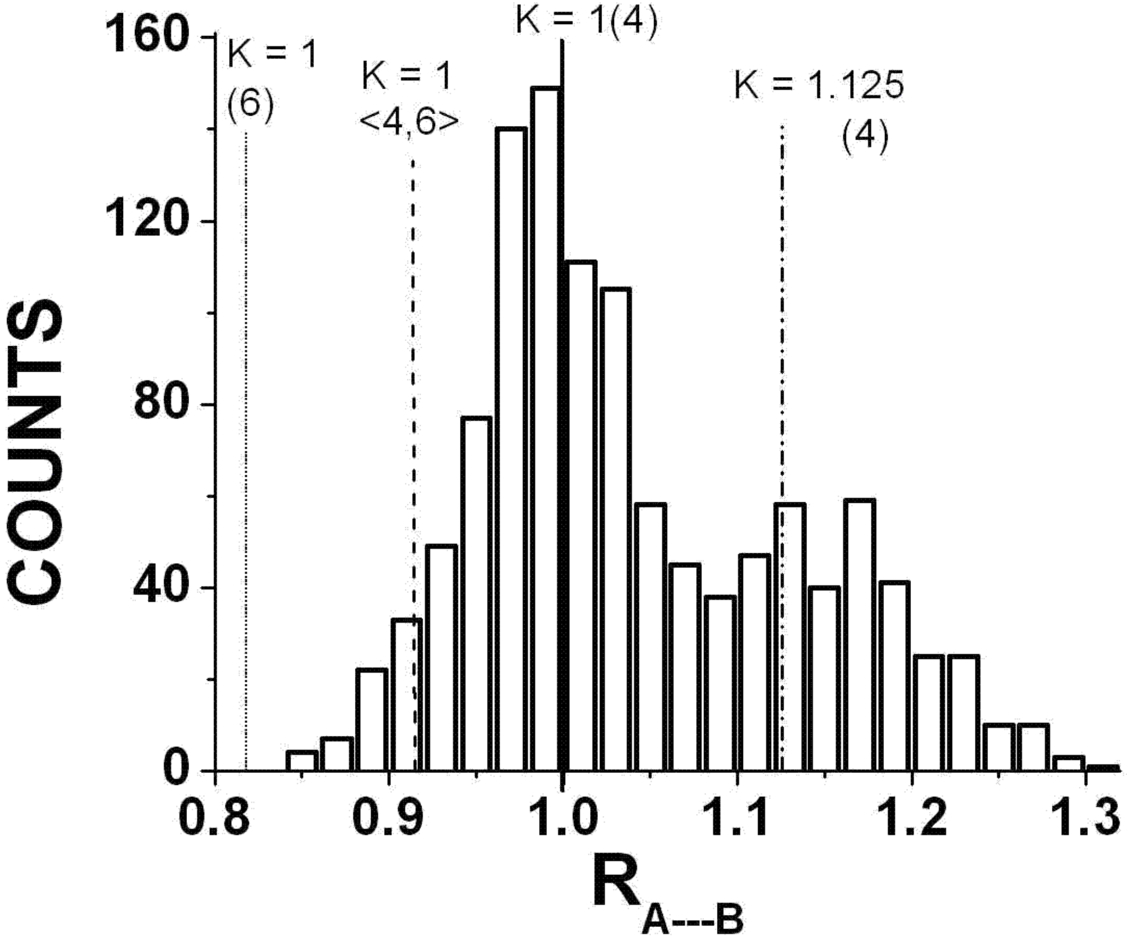

Fig 3. Histograms of the ratio R_{A---B} (= d_{A---B}(ob)/d_{A---B}(cal) of observed A¨B distance in crystals of various compounds of amino acids as compiled in the literature and the calculated A¨B distance using eqn 14 with K = 1 and r_{nZ}^{c} taken from Table 1. The vertical lines indicate the values calculated for the given values of K with the value of *N* given in brackets. The meaning of <4,6> is that it is the arithmetic average of values

expected for $N = 4$ and $N = 6$. Very short A$\cdots$B distances corresponding to $N = 6$ are not seen in these examples.

The calculated distances have been compared with those observed in compounds of biologically important amino acids by normalizing the observed A$\cdots$B distances with that calculated from eqn 14 with $N = 4$ and K = 1 and ε_{AA} or ε_{BB} calculated from eqn 15. The resulting ratio of observed and calculated distances is termed as R_{A---B}. We show in Fig 3 the histograms of the values of R_{A---B} of the distances observed using as a upper cut-off the distances given as the sum of van der Waals sizes in the CCDC tables. We see that there are two maxima around R = 1 and R = 1.125. The larger contributions may be attributed to "n-polar" (K = 1) sizes while the value of R_{A---B} for the other maximum is close to that are to be attributed to "neutral" or vdW (K = 1.125) sizes. There are no A$\cdots$B distances which are close to that expected for K = 1 and $N = 6$ although there are a few with A$\cdots$B distances that are close to that expected when an average value, <K> = (1 +1.125)/2 = 1.0625 (designated by $N = <4, 6>$ in Fig 3). As we shall see below The AHB hydrogen bond complexes with $R_{A---B} < 1$ are mainly those from the O$\cdots$N and O$\cdots$O distances.

When $N = 6$ and K = 1 in eqn 14 $R_{A---B} \sim 0.82$. For the O---O linkage the expected distance is nearly 236 pm (Table 2). A very short separation between carboxylate oxygens of only 230 pm has been claimed [31] for the active site of HIV-1 protease (PR). Usually a A$\cdots$B distance of ~ 280 pm in O$\cdots$H-O or O$\cdots$H-N complexes is an indication (K =1, N =14 in Table 2) of a normal hydrogen bond distance. These are usually associated with an enthalpy of formation which is close to -5 kcal/mol. Such hydrogen bonds are asymmetric as far as the location of the proton between the H and B atoms are concerned. Asymmetric proton locations persist even when O$\cdots$O distances are as small as 250-260 pm

4.2. OHN hydrogen Bond Complexes.

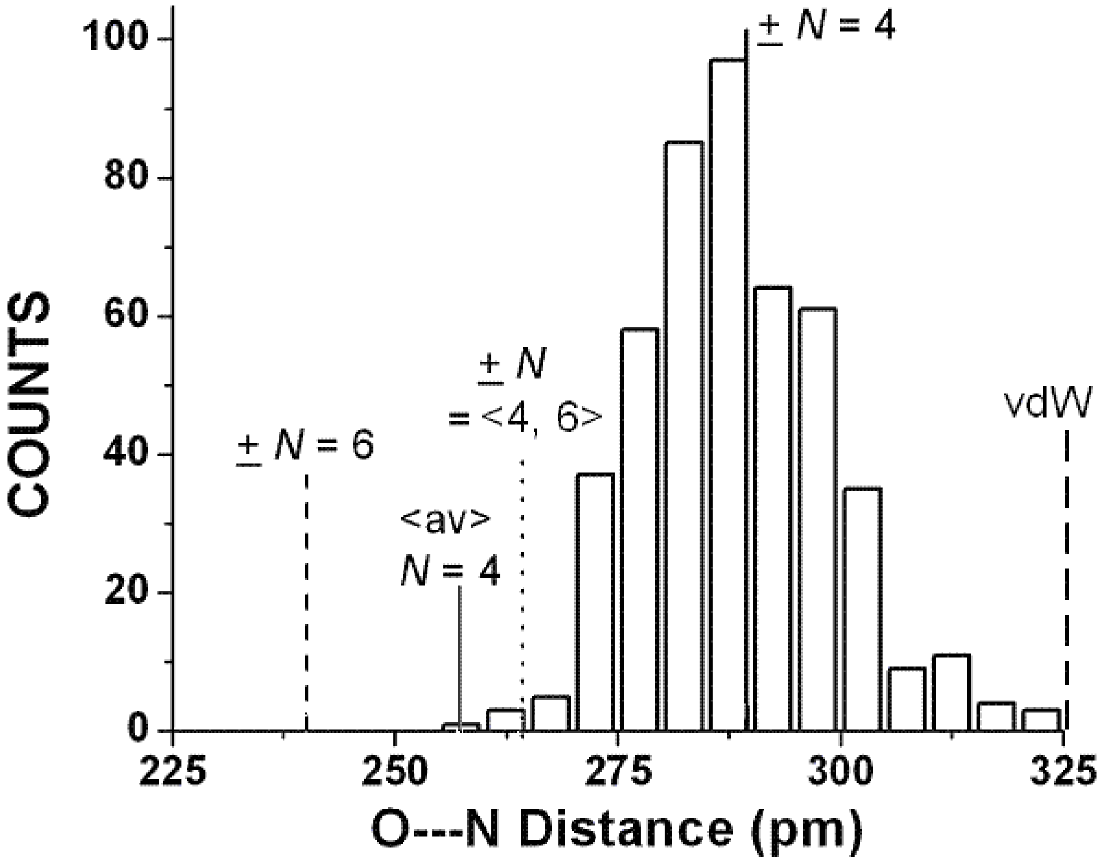

Fig 4. Histograms of O¨¨N distances in nominally O¨¨H-N hydrogen bond complexes of compounds of naturally occurring amino acids.

The O¨¨H-N hydrogen bond complexes are expected to be the most common in salts of biologically important amino acids that we focus on in this submission. The histogram of the O¨¨N distances in these hydrogen bond complexes are shown in Fig 4. Markers are also shown in the figure showing the expected distances for calculated values from eqns 11-14 with various values of *N* and K and with ε_{XX} calculated from eqn 15. It is seen from Fig 4 that the nominally O¨¨H-N hydrogen bond complexes have O¨¨N distances are peaked around that expected for the "normal" (*N* = 4, K = 1) O¨¨N distance.

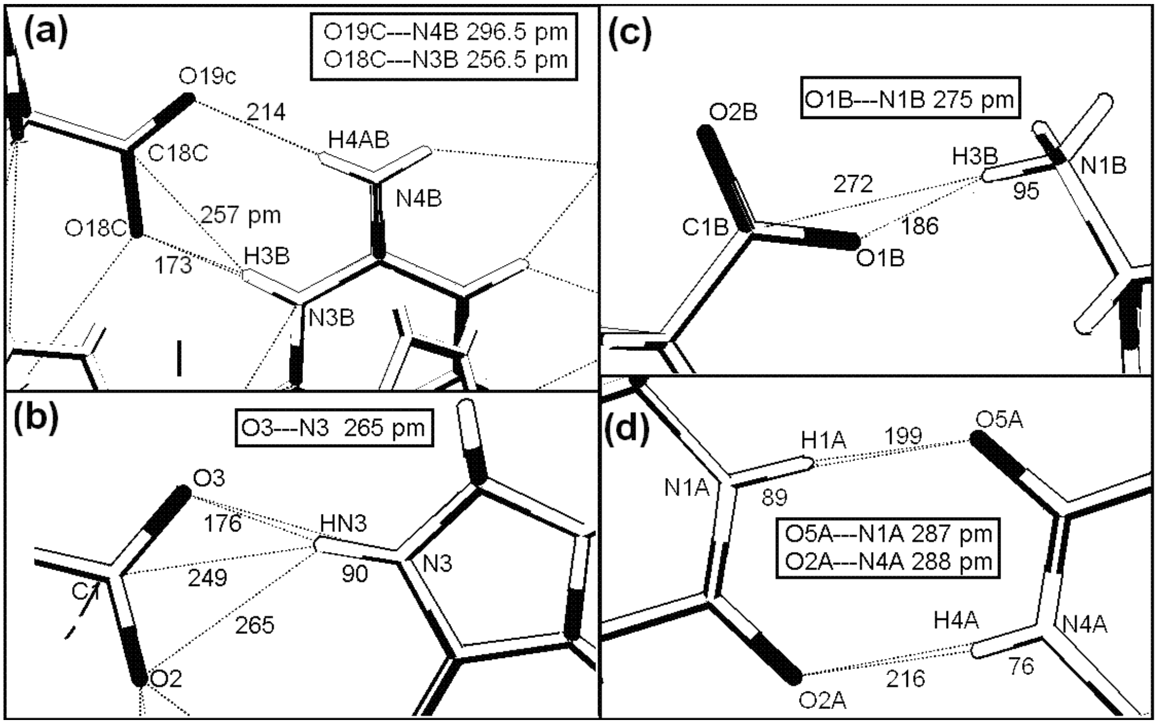

Fig 5. Contact geometry in nominally O···H-N hydrogen bond complexes. (a) N-[2-(4-amino-2-oxo-1,2-dihydropyrimidin-1-yl)propionyl]-1-phenylalanine [32/53']; (b) L-Histidylglycine Hydrochloride [33]; (c) 1:1 complex of D- and L-norleucine [34]; (d) cyclo-Glycyl-L-phenylglycine [35].

There is a shortening of the O···N distances, when the hydrogen atom in O···H-N hydrogen bond complexes are in contact with other atoms outside the complex and have contact distances less than that expected from the sum of their "neutral" (or vdW) sizes. These contacts are shown by dotted lines in Fig 5. As the number of such contacts with the hydrogen atom in the hydrogen bond complex increases the O···N decreases as is seen from an examination of Figs 5d-5b. There is no systematic change discernible in the N-H distances. The shortening of the O···N in figs 5b-5d may therefore be attributed to increase in the coordination number, *N*. The shortest O···N distance is seen (Fig 5a) in an intermolecular contacts between an O of the carboxylate group and NH group of the dihydropyrimidin group of N-[2-(4-amino-2-oxo-1,2-dihydropyrimidin-1-yl)propionyl]-1-phenylalanine [32]. In this contact the hydrogen-bonded hydrogen atom (H3B) has only one additional contact (with C18C, see fig 5a) with a C···H distance of ~ 257 pm which is close to the sum (257 pm) of the "n-polar" size of C and H atoms (Table 1). The shortened O···N distance in Fig 5a would not seem to be due to an increase in the coordination number, N, for the H.atom. At the same time the O(18C) and N(3B) atoms in the shorter O···N hydrogen bond of fig 5a are in shorter (less than vdW contacts) with other atoms in other molecules. This could result in a compressive pressure on the hydrogen bond complex and is reminiscent of that proposed by Cleland *et al* [7/17] for the formation of LBHBs during acylation of chymotrypsin.

5. More on Short Hydrogen Bonds and LBHBs.

The hydrogen bond between homo-nuclear atoms is especially interesting. One may consider the equilibrium between two hydrogen-bonded states such as

$$O_a\cdots H\text{-}O_b \leftrightarrows O_a\text{-}H\cdots O_b \qquad (18)$$

The initial and final states may be considered to be degenerate as long as the environments of the two oxygen atoms, O_a and O_b, are identical. In chemical terms this would translate into the two oxygen atoms having pK_a values close to each other. The important feature of eqn 18 is that the initial state is degenerate with the final state once there is no change in the nuclear position of the oxygen atoms relative to that of the hydrogen atom after the exchange. In this case there could be low-barrier "itinerant" hydrogen bonds with exchange of the H atoms between O_a and O_b atoms. The proton could be itinerant between the two structures in eqn 18 depending on the extent of pK_a matching. The tensegrity factor would then depend on the extent of sharing of the hydrogen atoms between the two oxygen atoms. The shortening of the $O\cdots O$ distance would then be governed by eqns 16a-16d and 17.

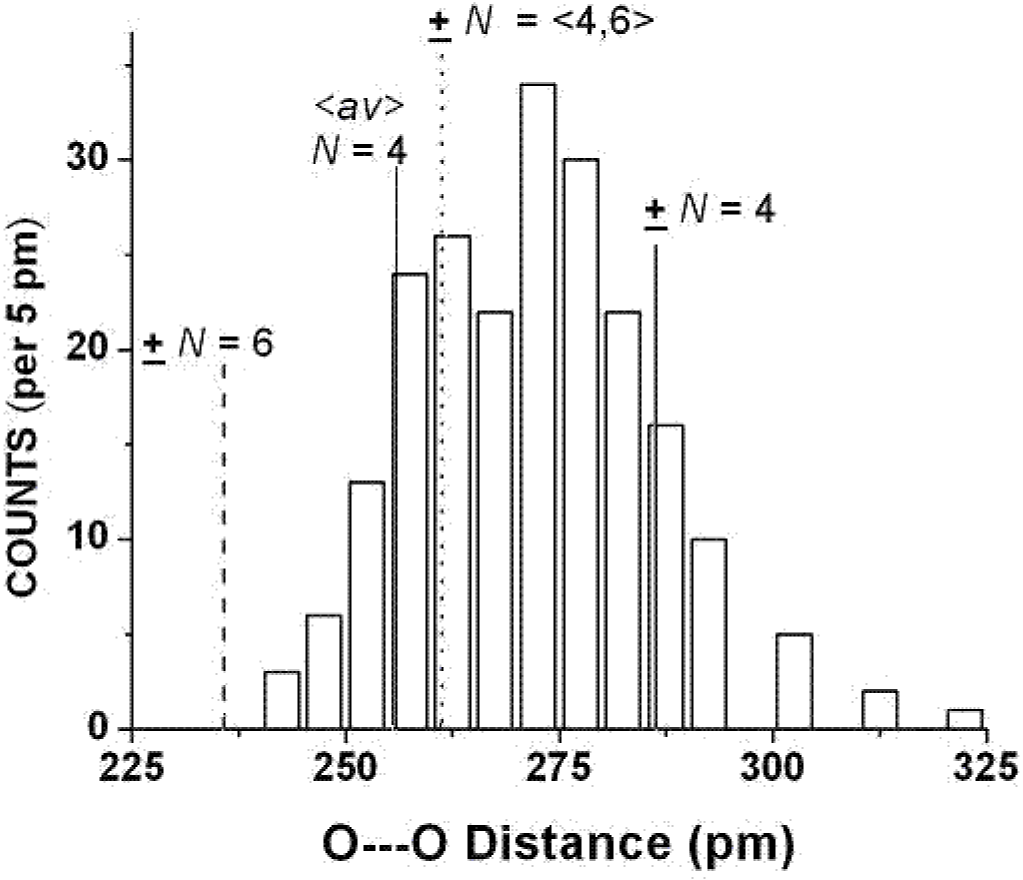

Fig 6. Histogram of $O\cdots O$ distance in OHO hydrogen complexes. Markers give expected values of the $O\cdots O$ separation (see Table 2) for various coorination numbers, N, for "n-polar" sizes without hydrogen sharing (indicated by ±) and for equal hydrogen sharing (indicated by <av>).

We have shown in Fig 6 the histogram of $O\cdots O$ distance of some representative compounds of α- amino acids. It is seen that, unlike the $O\cdots N$ distance in Fig 4, the maximum in the histogram occurs at a O···O distance that is considerably less than that calculated from eqns 11-15 with $N = 4$ and K = 1. This must be attributed to hydrogen sharing between the two oxygen atoms. There is a maximum around values expected for equal sharing (eqn 16a) of the hydrogen atom although there could be some influence due to an increase in N.

In order to further examine the reasons behind the shortening of the O···O distance we examine in Fig 7 some cases chosen at random with different O···O distances. Among the compounds studied here, the shortest O···O distance (~ 244 pm) is found in L-phenylalanine nitrate [36]. The number of contacts with the hydrogen atom (HD2A) in the hydrogen bond complex is quite large. The nominally "non-bonded" O···H distance is only 148 pm while the nominally bonded O-H distance is elongated to ~ 100 pm which is the longest O-H distance of the example shown in Fig 7. A similar shortening of the O···O distance is found in the the charged bis(L-proline)H$^+$ nitrate [40] in which the O···H distance is only 140 pm and the O-H distance is nearly 110 pm. The short O···O distance of ~242±2 pm in these compounds is therefore a combination of increase in number of close contacts which could be attributed to an increase in N as well as due to hydrogen atom sharing between the A and B atoms. As the coordination around H decreases on going from Fig 7a to Fig 7c, the O···O distance increases accompanied by a decrease in hydrogen atom sharing (an increase in the nominally O···H distance and a shortening of the O-H distance). We have also shown in Fig 7d hydrogen bonding in tricine [tris(hydroxymethyl)methyl]glycine [39] in which there are two OHO hydrogen bond complexes with similar coordination numbers and with O···O distances (269 ± 3 pm) which are slightly shorter than the calculated distance from eqns 11-15 ($N = 4$, K = 1) of ~ 286 pm. The OHO complex with the longer O···O distance also has the longer O···H distance. The extent of hydrogen sharing seems therefore to determine the O···O distance.

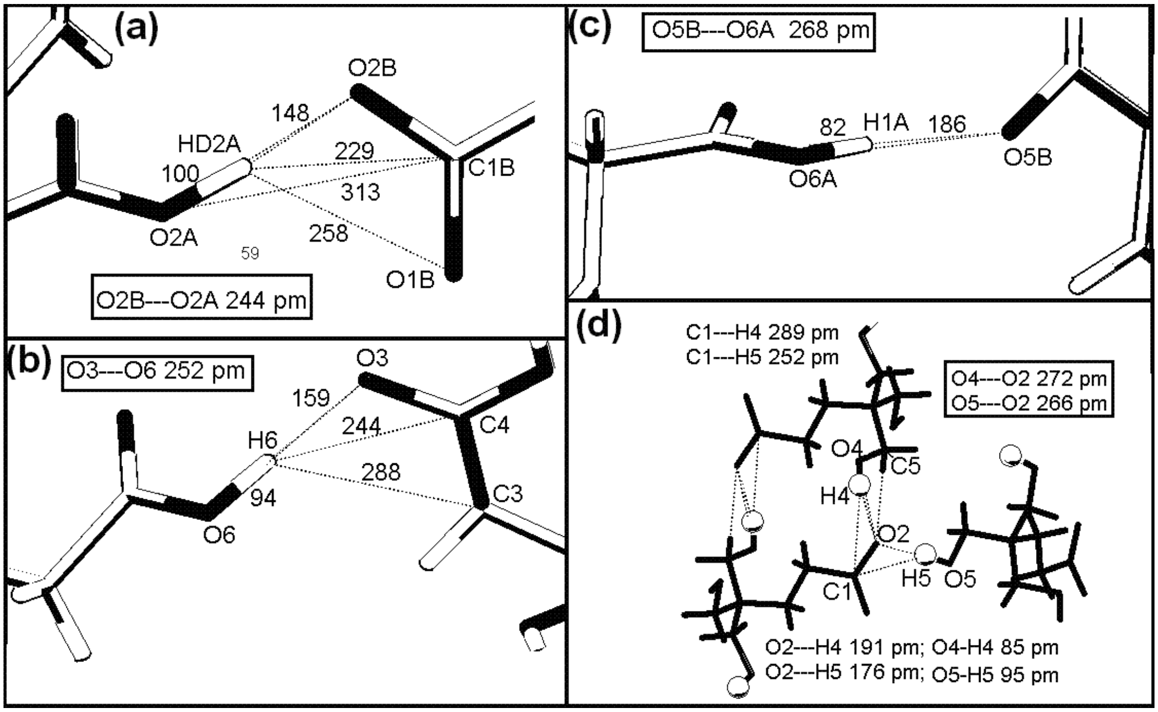

Fig 7. Contact geometry in nominally $O^{\cdots}H$-O hydrogen bond complexes. (a) L-phenylalanine nitrate [36]; (b) *N*-(Carboxymethyl)aspartic acid [37]; (c) Intermolecular hydrogen bonding of N-3,5-dinitrobenzoyl-L-leucine [38]; (d) N-[tris(hydroxymethyl)methyl]glycine (tricine) [39]

The critical feature of importance is the degeneracy of the initial and final states in eqn 18. This feature was first recognized as important in Zener double exchange [41] systems, as visualized in the manganites [42], for example. In mixed valence, M^{m+}-$M^{(m-1)+}$ systems (*m* is the number of valence *d* electrons, say) the equivalent electron transfer reaction has been written as

$$M_a^{m+}\text{-}M_b^{(m-1)+} \leftrightarrow M_a^{(m-1)+\cdots}(e)^{-\cdots}\, M_b^{(m-1)+} \leftrightarrow M_a^{(m-1)+}\text{-}M_b^{(m)+} \qquad (19a)$$

When the initial state is degenerate with the final state in eqn 19a, the energetically uppermost valence electron is itinerant between the atoms M_a and M_b. The individual valence states of the M atoms are not distinguishable (homogeneous mixed valence) when the measurement time is less than hopping frequency. In Zener double exchange systems, the spin of the electron plays an important role is plays an important part in introducing ferromagnetic coupling between M atoms when $m > 1$ as in the perovskite manganites [42]. This is because the electron-spin requires to be conserved during the exchange process as in eqn 19b below ($m = 4$; e.g., Mn^{3+}-Mn^{4+} in manganites).

$$M_a^{\uparrow\uparrow\uparrow\uparrow}\text{-}M_b^{\uparrow\uparrow\uparrow} \leftrightarrow M_a^{\uparrow\uparrow\uparrow\cdots}(e^{-\uparrow})\text{-}M_b^{\uparrow\uparrow\uparrow} \leftrightarrow M_a^{\uparrow\uparrow\uparrow}\text{-}M_b^{\uparrow\uparrow\uparrow\uparrow} \qquad (19b)$$

In very short hydrogen bonds (such as SSHBs or LBHBs) we may similarly distinguish between "homogeneous" and "heterogeneous" hydrogen bonds. In LBHBs a low barrier could presumably be associated with a "homogeneous" hydrogen bond in which the proton oscillates between the A and B atoms in a flat potential well as argued by Cleland *et al* [7].

Such spin- (or direction) conserving constraints for barrierless reactions are also present for energy transfer reactions in pigments. Förster's expression [43] for the energy transfer rate from donor to acceptor is dependent on the transition dipole moments of the donor and acceptor states. When the environments of the M atoms are different—say, with different coordination numbers or with different orientation of the O-H dipole—the M atoms in different valence states may become distinguishable (heterogenous mixed valence). Taking this analogy between electron-transfer and proton-transfer reactions further it would seem that linear O···H-O intermolecular hydrogen bond complexes or intramolecular O···H-O complexes in which the oxygen positions are fixed are more suitable for low-barrier processes.

In real molecules of biological importance the framework of the constituent atoms of the molecule could act as scaffolding that forces the A and B atoms in the AHB hydrogen bond complex to take up fixed positions and favour a low-barrier H exchange. The actual shortness of the hydrogen bond does not seem to be an important constraint or even an indicator for low barriers. It is possible that a large value of N around the hydrogen bond complex in the biological molecules reduces the O···O distance without necessarily correlating it to low barriers. In catalytic aspartases the active sites involving inner carboxylate oxygen atoms have hydrogen bond lengths between 260-287 pm. Warshel and Papazyan [44] suggested from energy considerations that low-barrier hydrogen bonds need not offer a catalytic advantage over ordinary hydrogen bonds.

In O···H-N bonds (prevalent in biological systems) the hydrogen atom is chemically bound to the less electronegative nitrogen atom so that the barrier to the H-O···N state from the O···H-N state may be less than the barrier to the O···H-N state from the O-H···N state. This makes the O-H···N hydrogen bond less likely to be a low-barrier hydrogen bond than the usual O···H-N bond. Steiner *et al* [45] have shown from neutron diffractions studies on adducts of 2-methylpyridine and pentachlorophenol with O···N distance being 258.8 pm the hydrogen atom position is sharply defined. The observed neutron O-H distance of 107 pm is among the longest O-H distance in nominally N···H-O hydrogen bond complexes that have been studied by neutron diffraction. One may therefore expect some contribution from hydrogen sharing. The hydrogen atom has short (less than vdW contact distances) contacts with a methyl hydrogen (d_{H---H} ~ 233 pm) and with an ortho- chlorine atom (d_{H---Cl} ~ 273 pm) so that the coordination around the H atom is effectively increased. Such increased coordination may also cause a shortening of the O···N distance.

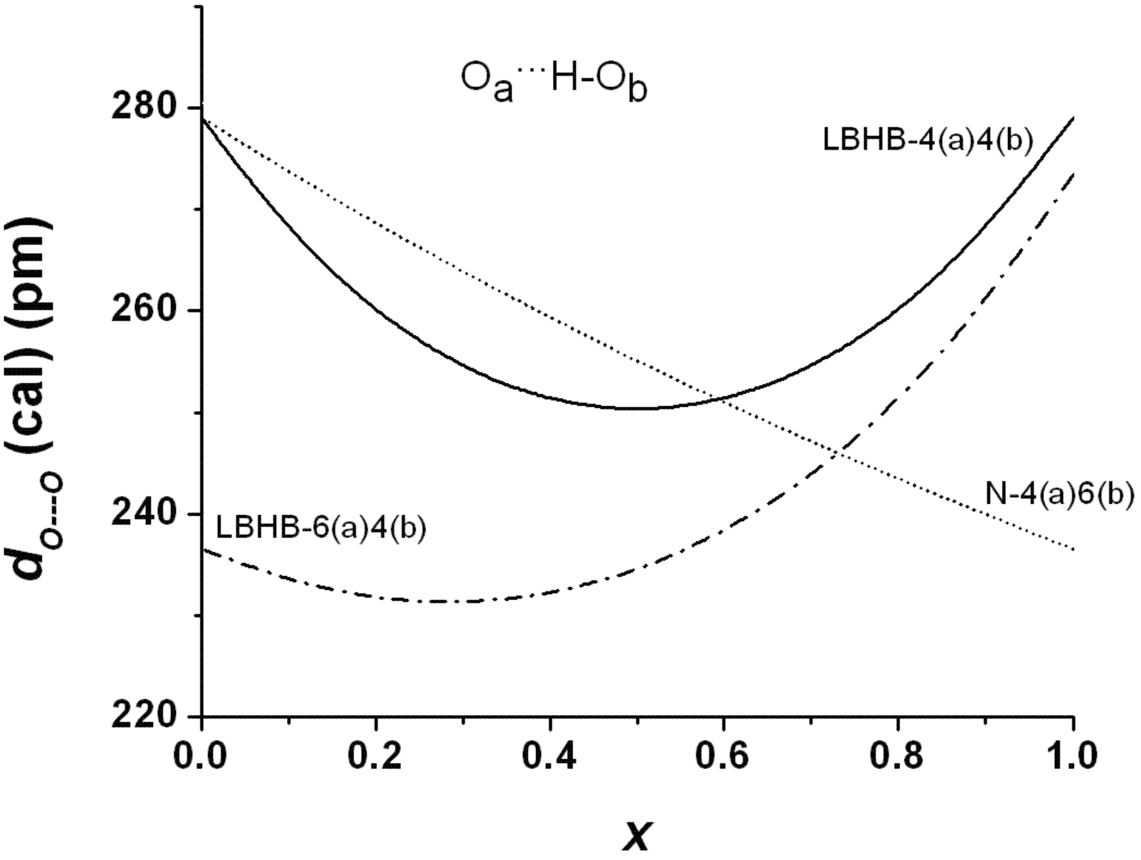

Fig 8. Changes in O···O distances in O···H-O hydrogen bond complexes as a function of the variation of some external parameter, *x*. Thick full line labeled as LBHB: From eqns 16c and 16d with $p = q$ and $N = 4$ in eqns 11-15. Dotted line. Value of *N* changed for O_a···H linkage from 4 to 6 and $N = 4$ for H-O linkage. Dots and dashes: From eqns 16c and 16d with $p = q$ and $N = 6$ for O_a---H and $N = 4$ for H---O linkage in eqns 11-15.

We have shown in Fig 8 the way O···O distance changes when the bonding with the hydrogen atom is shared between the donor and acceptor hydrogen atoms as in LBHB systems. When $N = 4$, the effect of changing p (= q) in eqns 16c and 16d results in the shortest O···O distance being at $x = 0.5$ with the shortest O···O distance being ~ 250 pm when $x = 0.50$. When $N = 6$ for one O---H linkage and $N = 4$ for the other in hydrogen-atom-shared LBHB systems the O···O distance is close to 232 pm for $0.5 < x < 0.7$ when x is the concentration of the O---H linkage with $N = 4$. Changes in the value of *N* from 4 to 6 for the non-bonded O···H linkage (without sharing of hydrogen atoms), for example, causes a monotonous decrease from ~ 280 pm to ~ 240 pm. Thus an increase in *N* and/or the introduction of hydrogen sharing between A and B atoms as in LBHB systems seem to be necessary for obtaining short O···O distances close to 240 pm. Whether such conditions are satisfied while accounting for the short O···O distance in of ~ 239 pm in $(H_5O_2)^+$ with a symmetric O---H---O bond would require further examination. Unlike discrete molecules or many inorganic solids the actual coordination geometry is not regular in the hydrogen bond complexes of biological systems studied here. This irregular coordination varies from one hydrogen-bond complex to another such that changes in *N* may be expected to quasi continuous

The role of LBHBs in other reactions could possibly have more potential than has been realized so far. For example, the well-known catalytic conversion of ketones to alcohols in the Meerwin-Ponndorf-Oppenauer-Verley reduction is now known to take place [46, 47] non-catalytically in supercritical isopropanol (at 300°C). From mechanistic investigation [46] of this reaction a six-membered intermediate of this reaction features a O¨H¨O linkage (see scheme 1) which may be presumed to have the same features as an intramolecular LBHB. So would the C¨H-C linkage.

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6. Other AHB Hydrogen Bond Complexes.

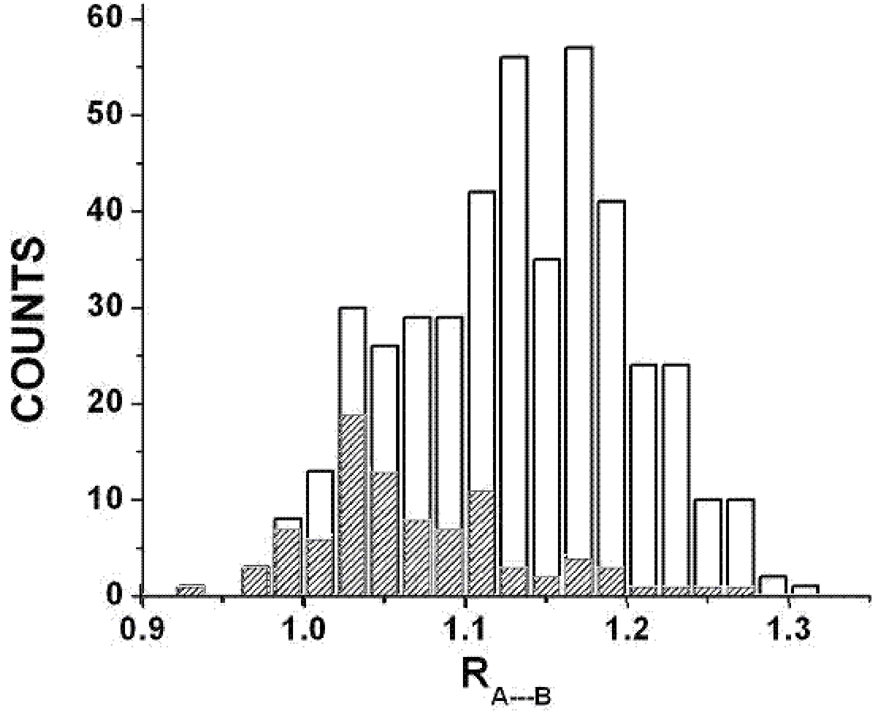

Fig 9. Histograms of $R_{A\text{---}B}$ ($d_{A\text{---}B}$(obs)/$d_{A\text{---}B}$(cal) from eqns 11-15 with $N = 4$ and K = 1) for all nominally A¨H-B hydrogen bond complexes except O¨H-N and O¨H-O hydrogen bond complexes. Hatched regions correspond to the historgrams in nominally N¨H-O, Cl¨H-O and Cl¨H-N hydrogen bond complexes.

We have shown in Fig 9 the histograms of the A¨B distances as the ratio $R_{A\text{---}B}$ (as in fig 3) in the nominally A¨H-B hydrogen bond complexes other than the O¨H-N and O¨H-O hydrogen bond complexes. The hydrogen bonded complexes other than O¨H-N and O¨H-O which have $R_{A\text{---}B}$ close to 1 (with predominantly " n-polar" character) are mainly the nominally N¨H-O Cl¨H-O and Cl¨H-N hydrogen bonds shown by hatched boxes in Fig 8). Among the A¨B distances with $R_{A\text{---}B} < 1$ are N¨O (1 out of 8), Cl¨O (5 out of 21), Cl¨H-N (3 out of 61), Cl---C (0 out of 23), C¨O (0 out of 45), C¨N (1 out of 44), C¨C (0 out of 28). Thus the A elements which are not N or O (fluorine has not been counted as there are not enough examples) usually have $R_{A\text{---}B} > 1$ and show a maximum in the distribution at values close to 1.125 ($N = 4$, K = 1.125 = $K_{neutral}$). We have shown the histogram for $R_{C\ldots C}$ in the main part of fig 6.

It is seen in Fig 9 that $R_{A\text{---}B}$ is peaked around $R_{A\text{---}B}$ = 1.125 and R ~ 1.17. The former would correspond to "neutral" or vdW distances calculated from eqns 11-15 with K = 1.125. The hydrogen bond complexes with $A^{\cdots}H$ distances considerably less than the "n-polar" size of A and H atoms ($CR_0^-(A) + 2a_H$) but with $A^{\cdots}H\text{-}B$ contact distances which give $R_{A\text{---}B}$ considerably greater than 1.125 may not be considered to be true hydrogen bonds. They usually occur as the weaker hydrogen bonds when there are many "acceptor" A atoms hydrogen-bonded with the same hydrogen as in the bi-furcated or trifurcated hydrogen bonds (see scheme II of [23/12']). Because of the many acceptor A atoms, the coordination number, *N*, of the hydrogen atom increases. An increase in *N* leads to a shortening of the distances as indicated by eqns 11-16.

7. Electronegativity of A and B atoms.

The above analysis indicates that "n-polar" (K = 1 in eqn 14) hydrogen bonds with $R_{A\text{---}B}$ ($d_{A\text{---}B}(\text{ob})/d_{A\text{---}B}(\text{cal})$ < 1 ($N = 4$, K = 1 in eqn 14) are likely only when B = O or N. When A = N or O, $R_{A\text{—}B} > 1$ especially when $B \neq$ N or O. In this case the observed distances correspond mainly to calculated "neutral" (K = 1.125) values indicating contacts similar to van der Waals complexes.

This change from "ionic" to "neutral" distances on interchange of A and B atoms for (B = O and N) is consistent with our model for interatomic distances (sec 2.2). For example, in calculating the H-B bond distance, the size CR_0^+ for the B atom is required (eqn 2, r_{nZ}^c (O or N) > r_{nZ}^c(H) = 0, Table 1). The size CR_0^+ is negative for oxygen (and fluorine) and close to 0 for nitrogen. Even in the case of nitrogen the size CR_0^+(N) is negative (~ - 6 pm) when we use the empirical size, r_G(N) = 0.26 a.u. and the relationship $CR_0^- = 2.25r_G - 37$ (in pm). The nucleus of an atom with a negative value of CR^+ is likely to be exposed to the valence electron of another atom [48]. The A atom in a Y'-A linkage of another molecule in a $Y'\text{-}A^{\cdots}H\text{-}B$ hydrogen bond complex is on the other hand associated with a negative charge ($r_{nZ}^c(Y') > r_{nZ}^c(A)$). A negative charge and hence the size CR_0^-(A) is to be associated with the A atom in the Y'-A linkage. There is thus a complementary size-charge synergy in CR_0^-(A) and CR_0^+(B) when B = O, F and N in $Y'\text{-}A^{\cdots}H\text{-}B$ linkages. This could be the fundamental basis for the "n-polar" (K = 1) description for describing most $A^{\cdots}B$ distances when B = F, O, and N. Such a condition has been, of course, expressed in the classic requirement that A be the more electronegative element in early descriptions [see 2/1, 23/12] of hydrogen bonding.

We have shown in Fig 10 a plot of the normalized $A^{\cdots}B$ distance, $R_{A\text{---}B}$ (as in Fig 9), *versus* the normalized $A^{\cdots}H$ distance $R_{A\text{---}H}$ (= $d_{A\text{---}H}(\text{obs})/d_{A\text{---}H}(\text{cal})$) for $O^{\cdots}H\text{-}C$ hydrogen bond complexes and $C^{\cdots}H\text{-}O$ hydrogen bond complexes. The calculated $A^{\cdots}H$ distance, $d_{A\text{---}H}$, is the sum of the "n-polar" sizes of the A and H atoms (= $CR_0^-(A) + 2a_H$). It is immediately apparent from Fig 10 that the $C^{\cdots}O$ contact distances in $C^{\cdots}H\text{-}O$ hydrogen bond complexes have little polar character being described mainly by K ≥ 1.125. The $O^{\cdots}C$ contact distances in $O^{\cdots}H\text{-}C$ hydrogen bond complexes, on the other hand, have more "n-polar" character. It is seen from Fig 10 that, $R_{A\text{---}B}$ becomes greater than 1.125 (signifying "neutral" A---B contacts) roughly when $R_{A\text{---}H}$ > 1.0 or when the

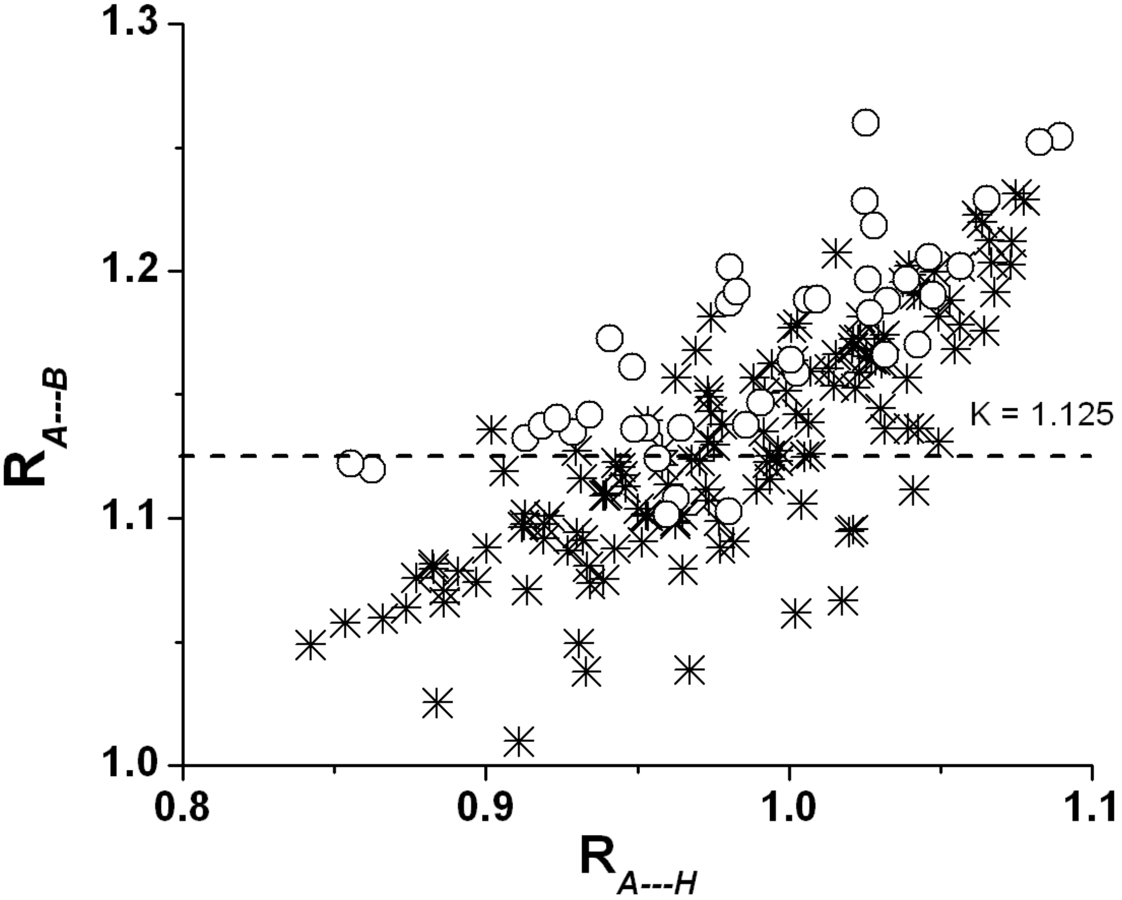

Fig 10. Plots of R_{A---B} (see legend of Fig 8) *versus* R_{A---H} (= d_{A---H}(obs)/(2.30r_{nZ}^{c}(A) + 4a_H) for C$^{\cdots}$H-O (circles) and O$^{\cdots}$H-C (stars) hydrogen bond complexes.

A$^{\cdots}$H contact distance is not completely described by "n-polar" character (for $N = 4$). One may thus characterize the C$^{\cdots}$H-O hydrogen bond complexes as weak and characterized by vdW interactions while the O$^{\cdots}$H-C hydrogen bond complexes have more "n-polar' character. We have come to this conclusion not from "distance fall-off" characteristics [25, 49] but simply from expected 1,3-distances using the molecular tensegrity model. The shortest O$^{\cdots}$C contact (~ 299 pm) is close to ~ 293 pm which is the sum of "n-polar" sizes of C and O in the complexes encountered in this study. It involves the C_5-H group in the imidazole ring and the oxygen of the carbonyl group of L-histidine methyl ester hydrochloride [50].

8. Systematic Changes in A$^{\cdots}$H and H-B Distances in A$^{\cdots}$H-B Hydrogen Bond Complexes.

Although the 1,3- A$^{\cdots}$B distance in A$\overset{\cdots}{-}$H-B hydrogen bond complexes are amenable to analysis in the molecular tensegrity model using eqn 14, for example, it may be necessary to understand the way the A$\overset{\cdots}{-}$H and H-B distances comply with changes dictated by the tensegrity of the A$^{\cdots}$H-B complex. After all, knowing the disposition of the hydrogen atoms would seem to be most necessary in allocating the nature of biochemical reactivity to the hydrogen bond complex. We expect first of all a fairly linear relationship between the A¨B distance, $d_{A\text{---}B}$, and the A¨H distance. $d_{A\text{---}H}$. We find that the best linear

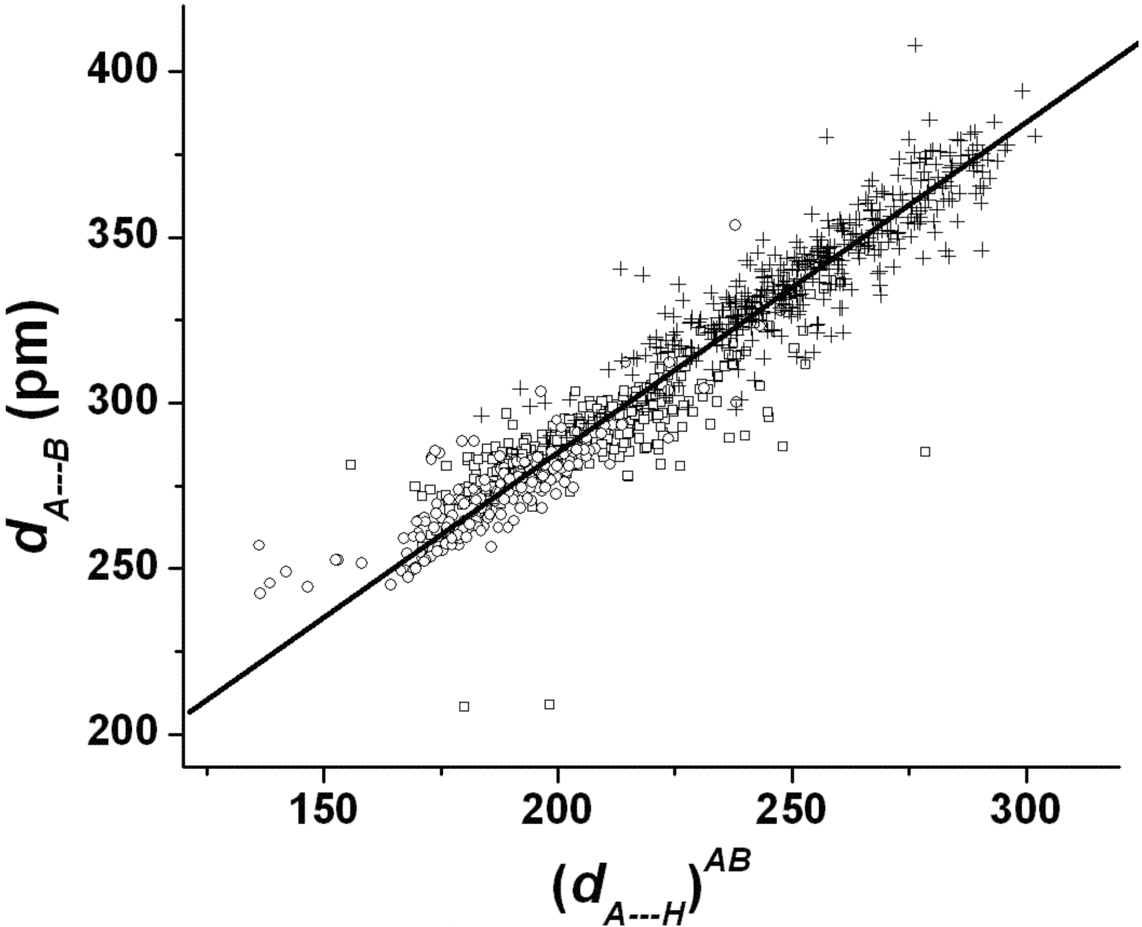

Fig 11. Plots of $d_{A\text{---}B}$ *versus* $(d_{A\text{---}H})^{AB}$ which is the component of $d_{A\text{---}H}$ along the A---B direction. circles: O¨H-O complexes; squares: O---H-N complexes; + sign: other A¨H-B complexes. Straight line is meant as a guide to the eye for unit slope.

relationship is observed (fig 11) between $d_{A\text{---}B}$ and the component, $d_{A\text{---}H}^{AB}$ (= cos(∠HAB)$d_{A\text{---}H}$) of $d_{A\text{---}H}$ in the $A¨B$ direction instead of the linear fit between $d_{A\text{---}B}$ and $d_{A\text{---}H}$. The best linear fit is given by (R > 0.93, SD = 12 pm)

$$d_{A\text{---}B} = 0.94 d_{A\text{---}H}^{AB} + 98 \text{ (in pm)} \qquad (20a)$$

while the best fit with unit slope is given by

$$d_{A\text{---}B} = d_{A\text{---}H}^{AB} + 85 \text{ (in pm)} \quad (R > 0.95, SD = 10 \text{ pm}) \qquad (20b)$$

$$\sim d_{A\text{---}H}^{AB} + 4a_H/5 \qquad (20c)$$

A free linear fit between $d_{A\text{---}B}$ and $d_{A\text{---}H}$ (R > 0.93, SD = 12 pm) gives

$$d_{A\text{---}B} = 0.90 d_{A\text{---}H}^{AB} + 105 \text{ (in pm)} \qquad (21a)$$

$$\sim 0.90 d_{A\text{---}H}^{AB} + 2a_H \qquad (21b)$$

The dependence of the intercept on the Bohr radius, a_H, of the hydrogen atom in eqns 20c and 21b is suggestive. The slope of unity in eqn 20b and the intercept of $2a_H$ in eqn 21b are perhaps more amenable to a facile interpretation. The relationships in eqns 20 and 21 highlight the synergistic behavior expected for the geometry of the A¨H-B complexes. These fits are also obtained (with the same slope and intercept) for the plots of $d_{A\text{---}B}$

versus $d_{A\text{---}H}$ except for lower R factor (R > 0.93) and higher standard deviation (SD = 12 pm).

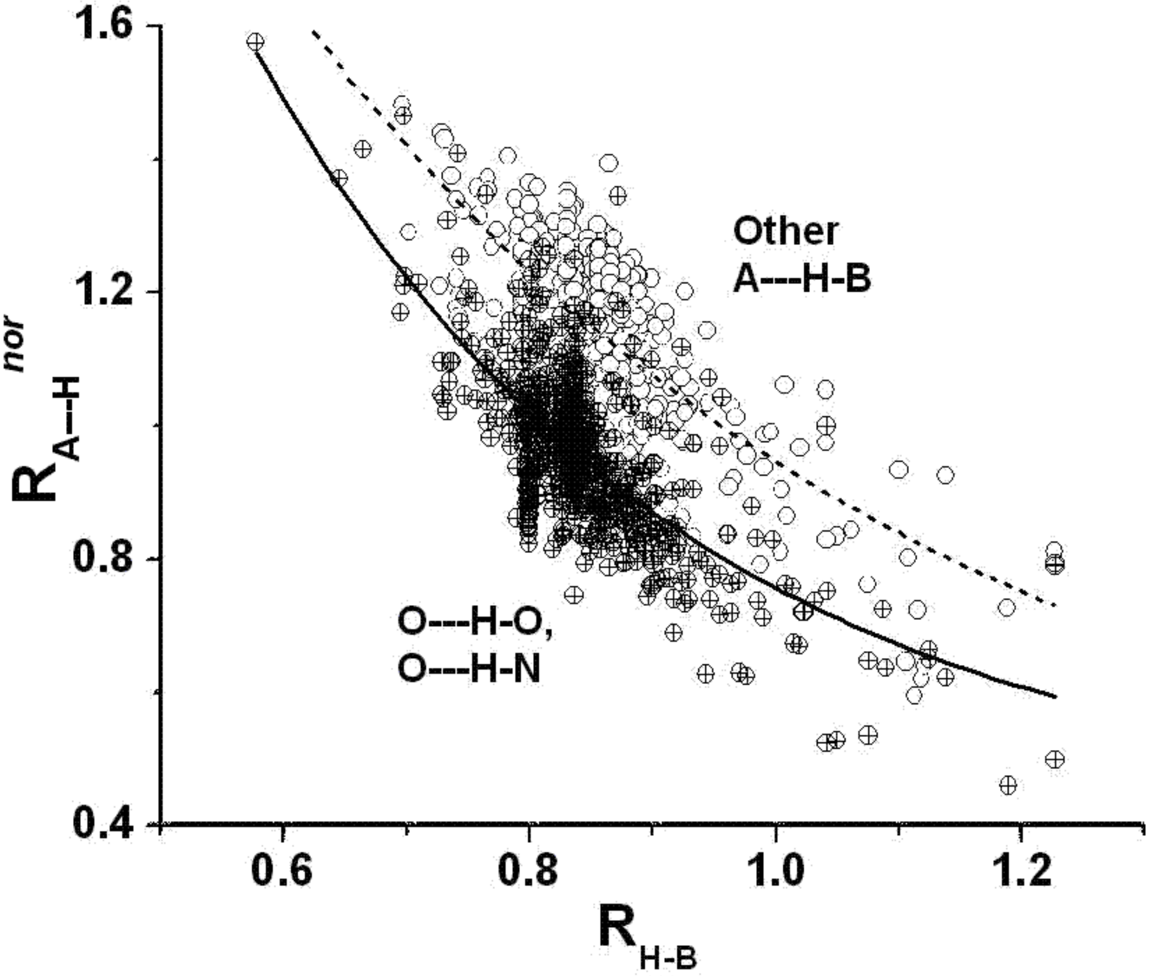

Fig 12. Plots of $R_{A\text{---}H}^{nor}$ (= $R_{A\text{---}H}/R_{H\text{-}B}$) *vs* $R_{H\text{-}B} = d_{H\text{-}B}/(2.144r_{nZ}^{c}(B) + 4a_H/3)$ and $R_{A\text{---}H} = d_{A\text{---}H}/\,(2.3r_{nZ}^{c}(A) + 4a_H)$. Circles with plus sign: O$\cdots$H-O and O$\cdots$H-N complexes with polar hydrogen bonds; open circles: others. Lines show best fit to an exponential decay of $R_{A\text{---}H}^{nor}$. Solid line: $R_{A\text{---}H}^{nor} = 0.42(\pm0.08) + 6.03(\pm1.44)\exp(-R_{H\text{-}B}/0.342(\pm 0.06))$; Dashed line: $R_{A\text{---}H}^{nor} = 0.33(\pm0.29) + 4.14(\pm1.15)\exp(-R_{H\text{-}B}/0.524(\pm 0.20))$.

One of the more well studied correlations in interatomic distances of A involves in A$\cdots$H-B hydrogen bond complexes the lengthening of the H-B bond distance as the A$\cdots$H distance is shortened. In neutron diffraction studies [23] of O$\cdots$H-O hydrogen bond complexes, for example, the O-H bond continuously elongates with decreasing O$\cdots$H-O distance until a symmetric $\text{O}\overset{\cdots}{-}\text{H}\overset{\cdots}{-}\text{O}$ geometry is reached at an O$\cdots$O distance of ~ 240 pm which is close to that calculated (see fig 8). The normalized A$\cdots$H distance, $R_{A\text{---}H}$ (= $d_{A\text{---}H}/\,(2.3r_{nZ}^{c}(A) + 4a_H)$) seems to decay exponentially with the normalized H-B distance, $R_{H\text{-}B}$ (= $d_{H\text{-}B}/(2.144r_{nZ}^{c}(B) + 4a_H/3)$. Thus, in the case of O$\cdots$H-O data [23] the best fit is obtained with

$$R_{O\text{---}H} = 0.45 + 230\exp(-R_{H\text{-}O}/0.139) \qquad (22a)$$

While for N$\cdots$H-O data the best fit is obtained with

$R_{N---H} = 0.43 + 75\exp(-R_{H-O}/0.18)$. (22b)

The corresponding normalized distances obtained from X-ray studies do not show straightaway a clear correlation. There does seem to be an exponential decay of the normalized value, R_{A---H}^{nor} (= R_{A---H}/R_{H-B}) of the A$\cdots$H distance with the normalized H-B distance, R_{H-B}, obtained from X-ray diffraction analyses roughly in the manner (Fig 12)

$R_{A---H}^{nor} = K(A_o + B_o(-R_{H-B}/KC_o)$ (23)

where $A_o \sim 0.3$, $B_o \sim 4.2$ and $C_o \sim 0.45$ and K = 1 for O$\cdots$H-O and O$\cdots$H-N for hydrogen bond complexes and K = 1.125 for the others. The parameters obtained from a best fit to an exponential decay are given in the legend of Fig 12 above along with the actual nature of the fit. As mentioned in the introduction, the X-ray diffraction results are necessarily different from neutron diffraction data and do not measure the same quantities. As such there is no justification for requiring universal parameters for A_o, B_o or C_o in eqn 23. The possible introduction of dual values of K in eqn 23 for "polar" or "neutral" hydrogen bond complexes is potentially satisfying. Apparently more experiments are required.

An important feature that emerges in Figs 11 is the nearly linear dependence of d_{A---B} on d_{A---H} (or R_{A---B} on R_{A---H}) which continues even when d_{A---H} of Fig 11 is greater than the sum of the "n-polar" sizes of the A and H atoms. This would indicate that there is a fundamental and universal aspect of the way the hydrogen atom of the donor H-B linkage interacts with the so-called acceptor A atom in the A$\cdots$H-B complex. The nature of the changes in Figs 11 and 12 indicate that although d_{A---B} is directly related to d_{A---H}, the extent of changes in d_{A--H} is dependent on the ability of the bonded H-B distance to accommodate such changes. This inter-dependence of d_{A---B}, d_{H-B} and d_{A---H} seems to constitute an integral part of the principles of molecular tensegrity and the way the whole defines the parts. It may be related in the way the proton is displaced from the centre of the hydrogen atom in the H-B linkage as in the atomic displacement model of Latimer [15] when the spherical atom approximation is not valid. In this case, the X-ray and neutron studies show complementary aspects of the structure of the A$\cdots$H-B hydrogen bond complexes.

6. Conclusions

This article is an attempt to obtain quantitative information on the nature of interatomic separations in A$\cdots$H-B hydrogen bond complexes as a function of the "polar" nature of the contacts with the hydrogen atom, sharing of the hydrogen atom between the A and B atoms as well as the influence of increasing coordination number, *N*, of the hydrogen atom. There is no dependence on DFT- or wave-function-based methodologies in this approach as we do not require minimizing energies to obtain a stable state of the molecule. Instead we approach the problem by applying [17-19] molecular tensegrity principles to molecules in a stationary state when the $\mu = 0$ condition is expected to hold [48]. Because of this it is sufficient to obtain atomic sizes that are consistent with this condition. The interatomic A$\cdots$B distance is obtained in this model without requiring an a priori knowledge of the A$\cdots$H and H-B distance. This conclusion is consistent in a way with the calculations of del Bene and Elguero [14] who find the two-bond NMR spin-spin coupling constants to be a monotonic function of the A$\cdots$B distance while the one-bond reduced NMR spin-spin coupling involving the hydrogen atom is a more complex function of the A···H or H-B distances. Our model would help in interpreting the experimental A···B distance in terms of the polarity of the contacts (value of K in eqn 15), extent of sharing of the hydrogen atom (value of p in eqn 16c) in bonding between A and B atoms as well as the number of contacts with contact distances less than that expected from "neutral" (or vdW).

The $\mu = 0$ condition is not uniquely defined by a fixed geometry or a unique set of atomic coordinates for an X-M-X' linkage in general or for A···H-B linkages in hydrogen bond complexes. The $\mu = 0$ condition is, however, expected for various different geometries in different environments. These geometries could be a function of a unique atom-specific size, r_{nZ}^{c} (Table 1) which may then vary for different kinds of bonding and environment. Once a given stationary state is reached, the final geometry does not depend on the way (the mechanics) this geometry is reached. Instead, it depends on the constraints on the various interatomic distances. The key spatial parameter in this case is the atomic size that is obtained from the $\mu = 0$ condition. For an X-M-Y linkage, these constraints depend on a tensegrity factor, $t^{00\pm}$, that is a measure of the matching of ideal bonded M-X (or M-Y) and 1,3- non-bonded X···Y "charge-transfer" distances for a give X-M-Y linkage. We have applied this model to more than 1000 A···H-B hydrogen bond complexes found in compounds of biologically important α-amino acids chosen at random from the literature in the last five years mainly. It turns out that the A···H distances are less than the sum of their "neutral" (van der Waals) sizes with K = 1.125 in eqn 10b.

The tensegrity factor is a simple function of the atomic sizes of the constituent atoms. Limiting values $t^{00\pm}{}_{\lim\to N}$ are obtained for different values of coordination number, N (= 4 or 6 in the present study). The calculated X···Y distance is then a simple function of the ration $t^{00\pm}/t^{00\pm}{}_{\lim\to N}$ for a given N and decreases with increasing N. The calculated distance is also a function of "n-polar" (ionic) or "neutral" (vdW) character of the X···Y contacts. We assume that the ideal non-bonded A···H distance (sec 2) is the sum of charge-transfer sizes, CR_0^-, of A and H atoms and that the ideal bonded A-H or H-B distance is, respectively, the sum of the charge-transfer bonded distance, $d_{AH}{}^{00\pm}$, of H and A atoms and $d_{BH}{}^{00\pm}$, of H and B atoms. The tensegrity factor for such hydrogen-bonded complexes is then defined (sec 3 eqns 13 and 14) and the expression for the A···B distance, d_{A---B}, is obtained (eqn 15) from the sizes KCR_0^-(A, B) of the A and B atoms with K = 1 describing "n-polar" (or ionic) sizes and K = 1.125 describing "neutral" (or what may be called vdW) sizes [21]. The possible A···B distances are tabulated in Table 2. The comparisons of calculated distances with experimental distances are expressed as histograms of their ratios, R_{A---B}, in various figures (Figs 4 and 6).

The O···H-O and O···H-N complexes have histograms of A···B distances that have their maximum corresponding to "n-polar" (K = 1) sizes for N = 4, while others have the maximum of their histograms close to the longer "neutral" (K = 1.125) sizes. We discuss the significance of low-barrier hydrogen bond complexes (LBHBs) and short hydrogen bond distances in terms of our model in section. The short A···B distances similar to those found in LBHBs may be described quantitatively in terms of hydrogen atom sharing between the two oxygen atoms. It is shortest (~ 250 pm, Fig 8) when the hydrogen atom is equally shared between the oxygen atoms. O$\cdots$O distances of nearly 240 pm in O$\cdots$H-O complexes would correspond to that calculated from eqn 15 when $N = 6$ for one of the O$\cdots$H linkages (see fig 5 and fig 8).

The role of electronegativity differences between A and B atoms are discussed in detail in sec 7, especially in the context of charge-transfer models for interatomic distances given in sec 3. This is discussed especially in the context of interchange of A and B atoms, as in, say, O$\cdots$H-C and C$\cdots$H-O complexes (Fig 10). The inter-dependence (Figs 11 and 12) of the A$\cdots$B distance with the A$\cdots$H distance and the A$\cdots$H distance with H-B distance, is discussed (sec 8) in terms of constraints that arise the hydrogen bond complexes are treated as tensegrity structures (Fig 7 and 8).

7. Appendix

This section has been included for the purpose of giving a tentative model for the formulae for interatomic distances as discussed in section 2. As such this model does not require a quantum theoretical approach. It simply assumes the existence of a spin (treated as a classical arrow or needle) and the way the total spin is conserved when two atoms are in contact. This condition for conservation of spin gives a geometrical factor from which the interatomic distances are obtained. The concepts introduced are new and will be treated in full detail elsewhere. It may suffice for the purpose of this communication in which we use the main conclusions. Because of this we have added this appendix.

The atom-bond transition (eqn A1) involves a quantum phase transition in which there is a two-doublet → singlet transition with a forbidden change of spin, characteristic of the spin-forbidden transition of biradicals during an inter-system crossover [51]. Thus, we may have

$$H_A\bullet + H_B\bullet \Leftrightarrow H_A e^o(\uparrow) + H_B e^o(\downarrow) \quad \text{(at instant of bond formation)} \qquad \text{(A1a)}$$

$$H_A e^o(\uparrow) + H_B e^o(\downarrow) + (e^- h^+) \Leftrightarrow H_A[\bullet(h^+)] + H_B[\bullet(e^-)] \equiv H_A[(e^o h^+)] + H_B[(e^o e)^-]$$
$$\Leftrightarrow H_B[\bullet(h^+)] + H_A[\bullet(e^-)] \equiv H_B[(e^o h^+)] + H_A[(e^o e)^-] \qquad \text{(A1b)}$$

The physical picture (eqns A4) describing such a transition, involves charge transfer from one doublet ($S = ½$) state to another to form a pair of opposite and spinless charges (eqn A1a). Such states may be formed on the absorption of the interaction energy represented by a virtual photon or electron-hole pair ($e^- h^+$) (eqn A1b). This leads to the formation of charge-transfer, spin-less, precursor quasiparticle states H($e^o e^-$) and H($e^o h^+$) that exist together only in the context of bonding [48, 52]. Like other quasiparticles in condensed matter physics [53, 54] these particles survive only in the context of its existence of a chemical bond and disappear completely when the atoms are taken apart. This condition resembles a "mystical" [1] text-book definition [55] of the hydrogen bond which states: '*Because the bonding depends on orbital overlap, the H-bond is virtually a contact-like interaction that is turned on when XH touches Y and is zero as soon as the contact is broken*'.

In condensed matter physics the quasiparticle usually is a low-energy collective excitation of a large number of particles (> 1) that emerges from strong interactions to behave as if they are non-interacting. This non-interacting condition is consistent with a free-atom-like $\mu = 0$ condition [48]. In the case of the formation of a chemical bond, the quasiparticle description only requires that the $\mu = 0$ condition is present even if only two particles are involved.

Much of this physical picture for the formation of a chemical bond may resemble the adiabatic winding argument proposed for the formation of charged solitons in polyacetylene [54, 56]. Such a crossover from non-interacting doublet "neutral" electrons to singlet charged states during the simplest chemical bond formation of the hydrogen molecule implies a transition across a phase boundary into a distinctly different state of matter and "*in the process doing some great violence to the ground state and low-lying excitations*" [54]. Thus, in describing the bonded state one requires to input additional parameters that take into account this phase transition specifically. Treatment of diatomic systems by molecular orbitals or other methods that use atomic orbitals or even atomic core sizes, r_{core}, may not satisfy this requirement. The classical chemists' "ball" and "stick" model ("hub" and "axle" in our nomenclature) specifically takes this into account since it is the "stick" ("axle") that is required by the bond-forming interaction that brings about the "phase transition". The H-H bond distance ("axle" distance), $d_{H\text{-}H}$, is obtained [48] as

$$d_{H\text{-}H} = 74 \text{ pm} = a_H^{eh} + a_H^{ee} = \varepsilon_{\mathrm{eff}}(4a_H/3) \equiv [D_H^- + D_H^+] = \varepsilon_{\mathrm{eff}}(2a_H - 2a_H/3) \qquad \text{(A2)}$$

when $\varepsilon_{\mathrm{eff}} = 1.05$. For $\varepsilon_{\mathrm{eff}} = 1$ we have $D_1^+ = 2a_H/3$ and $D_1^- = 2a_{\mathrm{H}}$ and $d_{H\text{-}H}(\varepsilon_{\mathrm{eff}} = 1) = 4a_H/3 \approx 70.6$ pm.

The "hub" sizes of eqns 3 are determined by the atom-specific size, r_{nZ}^{c}, and the coefficients $C^{\pm}$ when $F_S = 1$. We provide below purely geometrical arguments to show that $C_1^+ = \pi^{2/3} \sim 2.144$ and $C_1^- = \pi^{4/3}/2 \sim 2.300$ as used in eqn 3. The values of the coefficient $C_1^{\pm}$ have been related [48] to Mott's [57, 58] use of Thomas Fermi screening to obtain the critical concentration, n_c, at which a composition-controlled insulator-metal transition takes place in doped semiconductors, as an universal function of the Bohr radius, a_H*, associated with the dopant . The bonding pair of electrons may be considered to be characterized as being itinerant within the bond ("axle") dimension. The atom-bond transition may then be considered as a transition from a bound atomic state to an itinerant bond state as in an insulator metal transition at the critical concentration, n_c given by $n_c1^{/3} \approx 0.26a_H$*. This implies that the volume, V_c, occupied by the dopant at the critical concentration, is given by

$$V_c \approx 0.074(a_H^*)^3 \approx (0.74/\pi^2)(a_H^*)^3 \qquad \text{(A3)}$$

which is nearly one-tenth the close-packed fraction. If an effective size, a_{eff}, is defined such that $(4\pi/3)a_{eff}^3$ is the close-packed volume at the concentration n_c one obtains $a_{eff} = (a_H^*\pi^{2/3}) \approx 2.14a_H^*$.

Ganguly [59] has discussed the $1/\pi^2$ term in eqn A3 as a geometrical factor arising from a reduced probability of charge transfer with conservation of spin at the boundary of an insulator-metal transition (IMT). This would be a "spin representation" of the Thomas-Fermi screening and arises from a constraint on the way the spins on two sites require to be oriented with respect to each other before a charge is formed.

In a chemical bond between M and X atoms, the bonding valence electron of each atom may be treated as “neutral” spin ½ particle, •. The spins on these atoms require to be annihilated for spin-less charge to be created

$$\underset{\text{spin } (S = 0)}{\uparrow\bullet + \downarrow\bullet} \quad \Leftrightarrow \quad \underset{\text{charge } (S = 0)}{{}^{+} + [\uparrow\bullet\bullet\downarrow]^{-}} \qquad \text{(A4)}$$

Ganguly [59] has used the classical Buffon Needle problem [60] to show that probability, P_i, for charge-transfer (left to right of eqn A4) with conservation of spin is simply given by $P_i = 1/\pi^2$. If one takes the view that there is always a dynamic exchange of electrons in a chemical bond, one would require the probability of spin conservation in such exchange processes to be unity. Every such exchange requires conservation of spin. If the probability of conservation of spin is $1/\pi^2$, the volume of the “hub” has to be increased by π^2 or the size of the “hub” to be increased by $\pi^{2/3} \sim 2.144$. Just as the Thomas-Fermi screening length is the length within which the Coulomb potential is (exponentially) damped, one would require the size of the atom to be scaled by $\pi^{2/3} r_{nZ}^{c}$. The “hub” size $\pi^{2/3} r_{nZ}^{c}$, may then be treated as one in which the spin polarization in an atom due to the spin polarization of an external bonding valence electron is damped. For this reason we take

$$C_0^{+} = \pi^{2/3} \sim 2.144 \qquad \text{(A5)}$$

The value of $C_P = C_0^{+} = \pi^{2/3}$ is thus related to the probability of such spin-pairing as the first step before charge–transfer.

The probability of conservation of spin when two doublets are converted to charged singlets (left to right in eqn A4) is more than converting charged singlets to neutral doublets (right to left of eqn A4). This is always the case if there is extra stability of the right-hand side of eqn A4 due to the interaction between opposite charges. The vital distinction is that the forward (charge-creating LHS to RHS of eqn A4) direction involves the spin pairing of single-electron states. In the case of the charge annihilation (from RHS to LHS in eqn A4) of spin-less charged states $[\uparrow\bullet\bullet\downarrow]^{-}$, a pair of electrons is involved. The value of C_1^{-} is then related to the probability of spin-conservation when the pair of electrons in singlet charged state (RHS of eqn A4) is converted to the spin-paired doublet states (LHS of eqn A4). We simply assume that the probability of spin conservation when spin-correlation in the electron pair ($e_i e_j$) is imposed, is $2[\{(p^{i}{}_{//}{}^{\uparrow})(p^{j}{}_{//}{}^{\downarrow})\}\times\{(p^{i}{}_{//}{}^{\downarrow})(p^{j}{}_{//}{}^{\uparrow})\}] = 2/\pi^4$ where the factor 2 arises from the degeneracy of the two spin configurations of the electron pairs. The value of C_0^{-} is then given by

$$C_0^{-} = (C_0^{+})^2/2 = (\pi^{2/3})^2/2 \sim 2.300 \qquad \text{(A5).}$$

The actual implication of $C_0^{-} > C_0^{+}$ is that the probability of breaking the bond is less than that of making one, and which, therefore, marks the atom-bond transition.

From eqns A4 and A5 we obtain the theoretical charge-transfer distance, $d_{MX}^{\pm}$ as that given by eqn 3. It is for this reason that we consider eqn A3 to be the “ideal” value for the condition that $\varepsilon_{\text{eff}} = 1$ in eqn 1. The value of K = 1.125 for vdW sizes has been obtained [10] from the empirical fit between interatomic separation in rare-gas (RG = Ne, A, Kr, Xe) crystals and $2CR^{-}$(RG). Following arguments similar to those given above one may expect from the probability of charge exchange with spin conservation between two negatively charged states that $r_{vdW} \sim \{(C_1^{-})^2/2\}CR^{-}$ or $\sim 1.15CR^{-}$ or $K_{\text{vdW}} = 1.15$.

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Table 1. Atomic Sizes for some atoms relevant for this work.

Atom	r_{nZ}^{c} (a.u.)	$CR_0^{=}$ (pm)	CR_0^{+}(pm)	Atom	r_{nZ}^{c} (a.u.)	$CR_0^{=}$ (pm)	CR_0^{+}(pm)
H	0	105.6	-35.3	P	0.584	176.6	30.9
B	0.449	160	15.6	S	0.55	172.5	27.1
C	0.366	150.1	6.2	Cl	0.527	169.7	24.5
N	0.316	144	0.5	Se	0.648	184.4	38.2
O	0.282	140	-3.3	Br	0.625	181.6	35.6
F	0.256	136.7	-6.3	I	0.74	195.6	48.6

Table 2. Values of A$\cdots$B distances (in pm) in A$\cdots$H-B hydrogen bond complexes calculated from eqns 1-8 using various values of K and *N* and r_{nZ}^{c} from Table 1.

A$\cdots$B	d_{A---B} (cal) (pm)				
	N = 4 (A$\cdots$H-B)		*N* = 6(A$\cdots$H-B)		A$\cdots$H$\cdots$B K = 1 *N* = 4
	K = 1	K_{vdW}	K = 1	K_{vdW}	
F---F	281	315	231	259	250
O---F	283	318	233	262	253
N---F	285	321	235	264	257
C---F	289	325	238	268	262
O---O	286	321	236	266	256
N---O	288	324	238	268	259
C---O	291	328	241	271	265
Cl---O	305	343	250	282	286
S---O	307	345	252	283	289
P---O	310	349	254	285	295
Br---O	315	354	256	288	301
F---N	288	324	239	269	257
O---N	289	326	240	271	259
N---N	292	328	242	272	263
C---N	295	332	245	276	269
Cl---N	308	347	255	287	289
S---N	311	350	256	288	293
Br---N	314	353	258	290	304
P---N	319	358	261	293	299
O---C	296	333	247	278	265
N---C	298	335	249	280	269
C---C	301	339	252	284	274
Cl---C	314	354	262	294	295
S---C	317	356	263	296	298
S---S	319	359	265	300	322
Se---C	327	368	269	302	314